THE MEASUREMENT OF PERMEABILITY CHARACTERISTICS OF ANODIC FILMS ON ALUMINUM[1, 2]

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ABSTRACT

Techniques have been investigated for quantitatively studying the permeability of anodic aluminum oxide by measurement of rates of diffusion of salts through the film, rates of osmosis using the film as the membrane, rates of water transport through the film, and conductance of the film using salt solutions as electrodes. These techniques have been applied in an exploratory fashion to anodic film prepared by complete anodization of aluminum foil and to film separated from anodized aluminum by action of solutions of mercuric chloride.

Film liberated by the mercuric chloride solution is the less permeable. Films of equal thickness prepared in chromic and sulfuric acids are about equally permeable. Continued exposure to anodizing electrolyte after anodizing results in considerable increase in permeability, while "sealing" in boiling water causes a hundred-fold decrease in permeability. In contrast to their very unequal corrosive action, potassium nitrate and potassium chloride penetrate the film at about equal rates.

It appears as though the film is not entirely penetrated by pores but that a residual, comparatively impervious barrier layer exists in the film.

INTRODUCTION

The production of anodic film on aluminum by anodizing in solutions of chromic, oxalic, or sulfuric acids has been employed extensively to increase the corrosion resistance of aluminum and its alloys. Investigations of this process have, however, yielded little quantitative data on the permeability of bulk anodic film to ions and molecules although this must be of importance in determining corrosion resistance.

To extend such knowledge, four methods which give quantitative data bearing on permeability have been investigated and their application to

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anodic film has been explained. These involve: (a) rate of diffusion of salts through anodic film, (b) rate of osmosis using the film as the membrane, (c) rate of transport of water through the film, and (d) conductance of the film using electrolyte electrodes.

Two ways of usefully isolating anodic film as such seem possible. The anodic film may be separated from the metal or aluminum foil may be completely converted into anodic film. Action of aqueous mercuric chloride separates anodic film from its base (1, 2). Vollrath (3) has described a technique of complete anodization which involves raising the electrolyte level during anodization.

PREPARATION OF ANODIC FILM

Throughout this work aluminum foil 27.6 μ thick was used. Spectroscopically it was about 99.5 per cent pure, containing iron, silicon, and copper. Before anodizing, the foil was cleaned with chloroform and dipped for fifteen seconds into a 5 per cent solution of sodium carbonate at 86°C. A weight loss of about 1.8 per cent resulted.

Strips of foil 6 cm. wide were masked with microscope slides to avoid the destructive anodizing which otherwise results at the water line and anodized by one of two procedures.

(a) Chromic acid (1 part reagent chromic anhydride, 9 parts distilled water), 40°C., and 40 volts. This resulted in a current density of 7 milliamperes per sq. cm.

(b) Sulfuric acid (15 per cent by weight), 18°C., and a current density of 15 milliamperes per sq. cm. This required a voltage of about 17.

A thickness of 12 μ was desired for foils destined for complete anodization in chromic acid. The regular foil was anodized in sulfuric acid for an appropriate time. The oxide coating was then removed by a phosphoric-chromic acid solution (4) which leaves the metal unattacked. Very uniform thinning was possible.

Vollrath's (3) method was improved by first anodizing the foil in a normal manner until as little aluminum metal remained as practical. The process was then finished in a cell into which electrolyte was allowed to flow during anodization. By this means, the process was speeded and water line attack on aluminum metal was eliminated. The rate of rise of electrolyte was 2.5 cm. per hour. Stirring was essential for uniform anodization. In the case of the thin foil used in chromic acid anodizing, a frame of thin glass rod was required to avoid mechanical breakage.

Foil was washed three to four hours after the first anodization and sixteen hours after the final one in several changes of distilled water. After one hour, further washing resulted in negligible change in the conductance of the wash water even when protracted to forty hours.

Anodic film was 10–12 μ thick when prepared by complete anodization

in chromic acid solutions, and 40–42 μ thick when anodized in sulfuric. It was transparent but under microscopic examination dark specks aligned along the rolling lines were evident. Some of these were probably aluminum, some silicon. Over 90 per cent of the area seemed clear.

In the other process, aluminum foil was anodized and then treated with a solution of mercuric chloride. If the foil was immersed directly in a sublimate solution, an interface reaction which started at the broken edges of the foil led in several hours to the separation of the sheets of aluminum and anodic film. The inner face of the anodic film was incrusted, however, with considerable material which is apparently alumina produced by attack upon the aluminum metal. If the anodized foil was first sealed in place in the apparatuses to be described and then immersed in mercuric chloride solution, the anodic film-aluminum interface adjacent to the sublimate solution was separated as before. The aluminum metal was then slowly eaten away exposing the other anodic film. The face so exposed was in general very much less coated with debris and was free of it over considerable regions. The free anodic film was then washed in distilled water for four hours.

DIFFUSION OF SALTS THROUGH ANODIC FILM

Apparatus and Procedure

The apparatus used to determine the rate of diffusion of ionic solutes through anodic film resembles in principle the diffusion coefficient apparatus of Northrup and Anson (5). It is shown from the front and side in Fig. 1. A solution of suitable salt is placed on one side of a membrane of anodic film. Conductivity water is placed on the other. Diffusion of salt through the membrane is followed by periodic measurement of the resistance of the water.

To hold the membrane, a section of 15 mm. tubing was sealed at each end to 6 mm. tubing and a longitudinal slice was sawed from the larger tubing, parallel to the axis and far enough out to avoid cutting the 6 mm. tubing. The cut surface was ground flat to permit anodic film to be cemented in place with Thickol Cement EC601 (Minnesota Mining and Manufacturing Company). The foil is further masked by this material to give the desired area. The location of the foil is marked A in Fig. 1.

Loss of salt from the salt solution which occurs in consequence of its diffusion into the conductivity water is counteracted by passing solution through the inner cell during an experiment. Rod G nearly fills the feed tube from reservoir F. Upon removing it, the cell fills rapidly. Upon replacing it a slow flow of solution continues. Solution is removed from the apparatus by siphon H. The contents of the outer cell are kept uniform by an air stream released from a fine capillary located near the lower A in Fig. 1, and introduced through a tubulation adjacent to E.

The resistance of the solution in the external cell is read by means of un-

platinized platinum electrodes B, alternating current of 1000 cycles, and a standard Wien bridge with an oscilloscope detector. The cell constant was found to be 0.191 using 0.001 M potassium chloride. Polarization became serious only at salt concentrations greater than 0.002 M and occasioned no difficulty. All measurements were made at 25°C.

Results

Diffusion rates are presented in terms of moles diffused per sq. cm. of foil area per sec. per molar concentration fall across the membrane. Alternate runs were made with 0.1 M potassium chloride solution which served as a reference material.

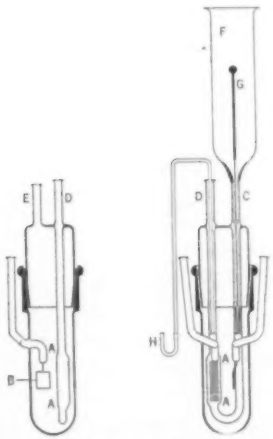

FIG. 1. Cell for measuring diffusion of salts through anodic aluminum oxide films.

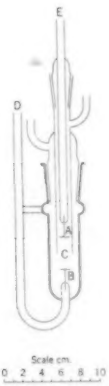

FIG. 2. Cell for measuring resistance of anodic film.

In Table I, data obtained on two sections of Foil A20 are shown. Section 3 was from the bottom of the sheet. During complete anodization in sulfuric acid, the centerline of Section 3 had remained in the anodizing bath for 111 minutes after complete anodization. Section 4, from the top of the sheet, had remained in solution for an average of 24 minutes after complete anodization. Foil thickness was 42 μ; areas were 2.24 and 2.14 sq. cm. respectively. Good straight lines were obtained in plotting moles diffused *vs.* time over two hour periods.

A run was made on section 4 of Foil A2, a piece similar in preparation to section 4 of Foil A20. The initial value of the diffusion rate in 0.1 M KCl was 1.8. It declined slowly during each run and after two thousand minutes was about 0.5. The plots of moles diffused *vs.* time showed slopes

diminishing with time during each run but the runs were longer than those on Foil A20. Upon plotting constants *vs.* time it appeared that corrected rates in 0.1 M and 1.0 M potassium chloride and 0.1 M potassium nitrate were equal to within 10 per cent.

Two series were run on sections of foil prepared by complete anodization in chromic acid. These were interrupted by a fracture of the delicate 12μ foils which must be handled with great care. With a section which had remained in chromic acid an average of 106 minutes after complete anodization, the diffusion rate with 0.1 M potassium chloride in the inner cell declined slowly over a period of 150 minutes from 1.93 to 1.82. In the succeeding run with 0.1 M potassium nitrate a value of 1.55 was found.

TABLE I. *Diffusion of salts through foil A20*
(Completely anodized in sulfuric acid)

Time*	Electrolyte	Diffusion rate‡
	Section 3	
min.		
66–250	0.1 M KCl	4.8
300–410	.1 M KNO_3	4.1
530–725	.1 M KCl	4.8
785–845	.5 M KCl	5.4
985–1110	.1 M KCl	4.9
1153–1220†	.5 M KCl	5.6
	Section 4	
75–250	0.1 M KCl	0.76
335–460	1.0 M KCl	.54
480–700	.1 M KCl	.48
785–950	.1 M KNO_3	.49
1015–1190	.1 M KCl	.46

* During time intervals not shown foil was being washed in distilled water.
† Following the previous run, the foil was masked ½ its previous area.
‡ In moles per sq. cm. per sec. per molar concentration fall across film $\times 10^9$.

Two runs were made on anodic film liberated *in situ* by the action of mercuric chloride solutions on but one face of foil anodized in chromic acid. Film prepared using ½ per cent mercuric chloride exhibited an initial increase in diffusion rate, 2.7 at 120 minutes and 4.4 at 380 minutes. That prepared in 2½ per cent mercuric chloride was less permeable and provided the only case in which the conductance of the conductivity water did not come to a steady state within a short time after first placing the inner cell in it. A slow but steady leaching was apparent. The diffusion rate after correcting for this was 0.06 and rose slowly. Upon exposing the foil to chromic acid solution for twenty minutes at 39° the rate was 7.7, rising rapidly thereafter to 30.

ELECTRICAL CHARACTERISTICS OF FILM

Apparatus and Procedure

The apparatus for measuring the resistance of anodic film immersed in solutions of electrolyte is shown in Fig. 2. A and B are platinized platinum electrodes. Anodic film is sealed to the inner tube at C by Thiokol Cement EC601.

The cell was filled with a given salt solution and its electrical characteristics were determined at a variety of frequencies (usually 60, 120, 180, 400, 1000, 2000, 5000, 10,000 cycles per sec.) over a period of time. The foil was then carefully broken out to the cement line and the measurements were repeated. A Wien bridge arrangement composed of an audio frequency oscillator, a General Radio Company Universal Bridge, Type 293A, and a cathode ray oscilloscope was used. Parallel resonant LC filters were inserted in the grid circuit of an auxiliary amplifier coupling the bridge to the oscilloscope. All measurements were made at 25°C.

The measurements represent the cell as an equivalent parallel resistance-capacitance circuit, R and C. With the foil cut out new values, R_1 and C_1, are obtained. From these, the equivalent parallel resistance and capacitance of the foil alone, R_2 and C_2, may be computed.

$$R_2 = \frac{(R - R_1)^2 + (RR_1\omega)^2(C - C_1)^2}{(R - R_1) - (RR_1\omega)^2(RC^2 - R_1C_1^2)} \tag{1}$$

$$C_2 = \frac{R^2C - R_1^2C_1(1 + R^2\omega^2C(C - C_1))}{(R - R_1)^2 + (RR_1\omega)^2(C - C_1)^2} \tag{2}$$

R_2 and C_2 are converted and listed per sq. cm. of foil area. At 5000 cycles and above, accuracy declines owing to residual capacitance and inductance in the bridge and to distributed capacitance across the cell.

An rms. voltage of 1.86 was normally applied to the bridge transformer. This resulted in the application of 0.30 volts to the network or, with equal arms, 0.15 volts across the cell.

There was little sensitivity to the setting of the condenser in the Wien network at the lowest frequencies when R was small. In such cases, the value of C_2 lacks precision.

Results

The data show the electrical characteristics of the foil to depend upon several factors:

(a) Method of preparing anodic film.

(b) When prepared by complete anodization, the length of time the section of foil had been in the anodizing bath after anodization had been completed.

(c) Electrolyte in which the foil is immersed and its concentration.

(d) Length of time in which the foil is immersed in the measuring solution.

(e) Upon changing the electrolyte, the identity of the preceding electrolyte.

The values of R_2 and C_2 depend upon frequency and, in certain cases, upon the voltage applied across the cell. The general behavior is complicated, and in spite of a considerable number of experiments, particularly on foils prepared by complete anodization, it has not been fully elucidated.

TABLE II. *Equivalent parallel resistance of Foil A25 (completely anodized in chromic acid) as a function of frequency*

Section number	Solution	Time	R_2 in ohms per sq. cm. at frequency of						
			60	120	180	400	1000	2000	5000
		hrs.							
2	0.01 M KCl	3.3	176	176	176	174	175	174	168
2	.1 M KCl	4.7	39.5	39.5	—	39.5	39.3	39.3	39.3
6	.01 M KCl	0.6	708	706	703	701	697	681	615
6	.1 M KCl	3.8	210	209	209	208	209	210	206
6	.01 M KCl	73	979	975	979	975	961	912	789

TABLE III. *Equivalent parallel capacitance of Foil A25 as a function of frequency*

Section number	Solution	Time	C_2 in microfarads per sq. cm. at a frequency of						
			60	120	180	400	1000	2000	5000
		hrs.							
2	0.01 M KCl	3.3	0.119	0.107	0.108	0.098	0.091	0.090	0.087
2	.1 M KCl	4.7	.149	.154	—	.109	.103	.102	.100
6	.01 M KCl	0.6	.106	.095	.091	.087	.085	.083	.081
6	.1 M KCl	3.8	.120	.160	.098	.091	.088	.085	.084
6	.01 M KCl	73	.107	.102	.099	.097	.095	.093	.087

Two experiments typical of those on foils prepared by complete anodization are shown in Tables II and III and in Fig. 3. Immersion in the anodizing electrolyte following complete anodization continued ninety-one minutes for section 2 and twenty-nine for section 6. Initial immersion in 0.01 M potassium chloride was followed by 0.1 M potassium chloride and then 0.01 M solution again. Immersion in the latter was protracted several days in the case of section 6. Resistances and capacitances at 60 cycles are shown in Fig. 3, their variation with frequency in Tables II and III at a few selected times. Table IV presents the dependence of R_2 upon electrolyte in terms of the ratio of R_2 in the solution to R_2 in 0.01 M KCl at the nearest appropriate time. For this purpose, measurements were made at suitable intervals with 0.01 M potassium chloride solution. Films prepared by complete

anodization generally exhibited a slow increase in resistance with time of immersion in the cell, but ordinarily this was not very large except over

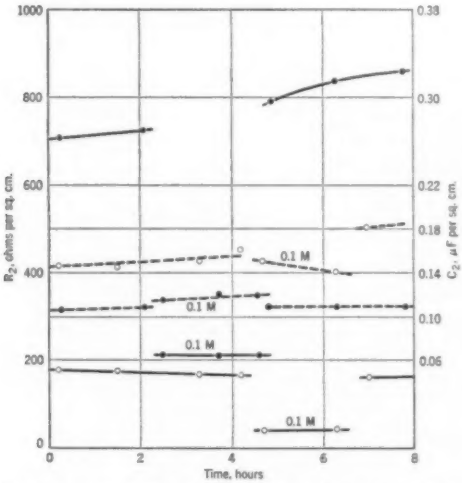

FIG. 3. Electrical characteristics of Foil A25 at 60 cycles, 25°C. Empty circles, section 2; full circles, section 6. Solid lines, resistance; dashed lines, capacitance. Electrolyte, 0.01 M KCl except where shown as 0.1 M KCl.

TABLE IV. *Ratio of equivalent resistance to resistivities*

Foil	Section	Time in bath after complete anodization	Solution	$\frac{R_2}{R_2\ (0.01\ M\ KCl)}$	$\frac{\rho^*}{\rho\ (0.01\ M\ KCl)}$
		min.			
A25†	2	91	0.1 M KCl	.22	.110
			.01 M Na-β-$SO_3C_{10}H_7$¶	5.6	1.90
	5	86	.004 M $MgCl_2$	1.45	1.49
			.005 M K_2SO_4	1.94	1.05
	4	34	.1 M KCl	.26	.110
			.004 M $MgCl_2$	1.2	1.49
	6	29	.1 M KCl	.29	.110
A26†	2	83	.1 M KCl	.24	.110
			1.0 M KCl	.040	.0126
A21‡	2	112	.1 M KCl	.30	.110
			.005 M K_2SO_4	2.93	1.05

* ρ = resistivity of solution.
† Completely anodized in chromic acid.
‡ Completely anodized in sulfuric acid.
¶ Sodium naphthalene-β-sulfonate.

periods of twelve hours or more. In addition, there was a drift following change of salt solution, the first fifteen minutes of which was confused by

lack of temperature equilibrium and was ignored. Upon returning to 0.01 potassium chloride following potassium sulfate or sodium β-naphthalene sulfonate solutions, R_2 at 60 cycles usually drifted down toward limits above former values of R_2. Owing to these considerations no great precision is attached to the ratio of R_2's given in Table IV.

With foils anodized in sulfuric acid there was an initial upward drift following 0.1 M potassium chloride solutions. The opposite was true upon following the 0.01 M solution with 0.1 M. Otherwise behavior of films prepared in the two acids was similar. The value of R_2 under comparable conditions was about twice to thrice greater for sulfuric acid anodized foil.

In contrast to considerable changes in R_2, the value of C_2 at 60 cycles differed but little from case to case. For the film anodized in chromic acid, the value was about 0.10–0.11 microfarads per sq. cm. in 0.01 M potassium chloride for the sections of shorter extra immersion in the anodizing bath and 0.13–0.14 for those of the longer. Effect of potassium chloride concentration was negligible. In 0.005 M potassium sulfate C_2 was 20–30 per cent lower and in magnesium chloride solutions, perhaps 10 per cent lower. In general C_2 changed little with time. C_2 was about thrice as great in the case of sulfuric acid anodized foil.

The dependence of R_2 and C_2 upon frequency for anodic film prepared by complete anodization in general resembled the results presented in Table II. Usually, the greater R_2 the greater the value of dlnR/df. This was not true for C_2.

The investigation of anodic film liberated by the action of mercuric chloride was less extensive. Three samples prepared by the direct action of a 0.5 per cent solution on foil anodized in sulfuric acid were studied. These were 16μ thick. Results were not consistent. Two gave values of R_2 twice and one a value one-quarter that of the film isolated by complete anodization (extrapolated to zero time of extra immersion). In the first case the capacitance was less, in the other greater. Such irregularity might be expected from the mechanism of action of mercuric chloride in this case. Film isolated by the action of the mercuric chloride solution on the anodized foil sealed *in situ* offers a much more promising material. One run was made on a section of chromic acid anodized film, thickness 10μ isolated by 2½ per cent mercuric chloride solution. R_2 measured initially in 0.1 M potassium chloride declined somewhat and reached a value of 4500 ohms per sq. cm. after two hours. Upon changing to a 0.01 M solution the resistance rose in twenty-two hours more from 16,000 to 49,000. During this period if current at 60 cycles was passed continuously through the cell (instead of just at measurement), R_2 declined by 6000 ohms. Upon halving the voltage, R_2 rose 4,000 ohms. The behavior

was reproducible. Changes were not instantaneous but required thirty minutes to an hour for completion. C_2 remained constant at about 0.2 throughout these changes. Similar behavior was exhibited in general by the high resistance foils and to a small extent even by the low resistance ones.

Section 1 of Foil A21 prepared by complete anodization in sulfuric acid (112 minutes extra immersion) was sealed by immersion in boiling water for fifteen minutes. The value of R_2 at 60 cycles rose from 375 to 44000 ohms per sq. cm. C_2 fell from 0.48 to 0.040 microfarads per sq. cm. Similar behavior was exhibited by a section of foil completely anodized in chromic acid.

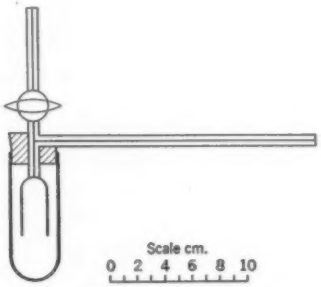

FIG. 4. Osmometer

The "sealed" foils exhibited a much greater proportional change in both R_2 and C_2 with frequency. This was also true of the film isolated by mercuric chloride from sulfuric acid anodized foils. In the case of film isolated *in situ* from chromic acid anodized foil, the rate of change of R_2 with frequency was large but that of C_2 was nearly zero.

OSMOSIS THROUGH THE FILM

Apparatus and Procedure

The apparatus employed in measuring rates of osmosis is shown in Fig. 4. The largest diameter tube provides a container for pure water. The tube within this is closed by sealing anodic film across its end. The inner reservoir thus provided is filled with a solution of sucrose by means of a pipette inserted through the 2 mm. straight bore stopcock so that the sucrose solution penetrates about 1 cm. into the calibrated horizontal capillary which is provided with a scale. The cell is thermostated at 25°C. and volume increase *vs.* time is recorded. By this arrangement, osmosis proceeds at a low constant head. It was possible to use anodic film but 6μ thick. Errors consequent to change in head, such as distention of the

membrane, are avoided. Except in one experiment, a 0.2 M solution of sucrose was used.

Results

Accompanying the flow of water into the sugar solution was a reverse flow of sugar into the water as was shown by test with Tollen's Reagent. Sugar was apparent after a few days. This has not been investigated quantitatively.

Table V shows the results of runs on anodic film prepared by complete anodization. Duplicate experiments were usually run and showed reasonably good agreement. Following the completion of some runs, the solu-

TABLE V. *Rates of osmosis through completely anodized foils, 0.2 M sucrose solution, 25°C.*

Foil	Section	Time in bath after complete anodization	Initial rate, cc./cm².day	Duration of run
		min.		*days*
A31 (H_2CrO_4)	1	24	0.015	6
	2	24	.0125	6
	3	76	.073	3
	4	76	.053	1
	5	24 (sealed)‡	<.0002	7
A37 (H_2CrO_4)	1	22	.0094	7
	2	100	.078	2
A35 (H_2SO_4)	1	14	.0031*	5
	2	14	.0033*	7
	4	65	.020	5
	5	62	.020	5
A2 (H_2SO_4)	1	107	.018†	7–13

* Rate increased initially, reaching maximum on 3rd day. This value is recorded here.
† Computed from rates of 0.1 M and 0.3 M sucrose solution.
‡ Sealed 20 minutes in boiling water. Rate of osmosis unmeasurable.

tion and water were renewed and the runs continued. For sections 1, 3, and 4 of Foil A31, the rates were then 0.0016, 0.070, and 0.057 cc. per sq. cm. of foil per day; for sections 1 and 2 of Foil A37, 0.020 and 0.071; and for sections 4 and 5 of Foil A35, 0.0175 and 0.015.

The course of experiments on two sections of Foil A31 is shown in Fig. 5. The upper curve refers to section 3 which had remained in the anodizing bath an average of seventy-six minutes after complete anodization, the lower one to section 1 of twenty-four minutes extra immersion. After three and six days respectively, the water and sugar solutions were renewed and the runs continued. The second series are shown with dashed curves, the volume increases being added to those of the first series.

In all cases the behavior of foil which had remained for longer times in

the anodizing bath resembled that shown in Fig. 5. In the case of the shorter extra immersion, the sulfuric acid foils exhibited an induction period. The greatest rate of osmosis was reached during the interval

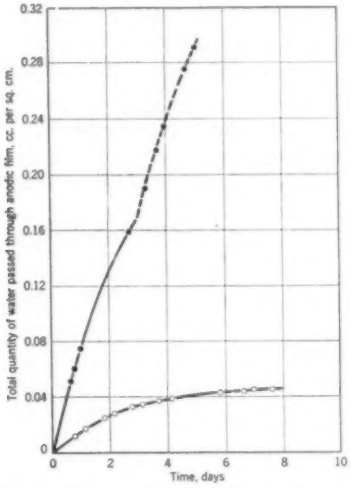

FIG. 5. Osmosis through Foil A31, 0.2 M Sucrose, 25°C. Empty circles, Section 1, full circles, Section 3.

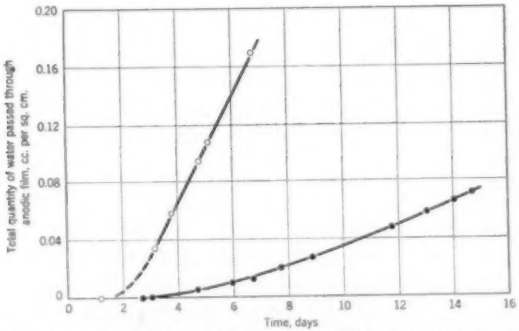

FIG. 6. Osmosis through Foils A40 and A41, 0.2 M Sucrose, 25°C. Empty circles, Foil A40, Section C, liberated by 2½ per cent $HgCl_2$; full circles, Foil A41, Section A, liberated by 5 per cent $HgCl_2$.

between forty-eight and sixty-four hours. Following this the rate declined, reaching one-sixth of the maximum by the seventh day.

The section of Foil A31 which was sealed exhibited no detectable osmosis during a week.

The effect of sugar concentration was studied on two similar sections of Foil A2. The average daily rate for the first five days with 0.3 M sucrose was 0.028; with 0.1 M, 0.0092 cc. per sq. cm. per day.

Fig. 6 exhibits the behavior of anodic film isolated by the action of mercuric chloride. Aluminum was anodized in chromic acid solution for seventy minutes. Sections of this were sealed to the osmometers and the film isolated *in situ*. A 2.5 per cent solution was used for Foil A40 and a 5 per cent one for Foil A41. Runs were in triplicate and agreed well. One of each is shown in Fig. 6.

PERMEABILITY OF ANODIC FILM TO WATER

Many methods of measuring the flow of water through a membrane into dry air have been described. Some preliminary measurements were made on a device resembling the osmometer of Fig. 4 in which the inner portion was filled with pure water to the end of the capillary and a jet of air was played upon the anodic film.

With less permeable films the rate of loss of water, as measured by the retreat of the meniscus in the calibrated capillary, was independent of air flow beyond a certain rate of flow. With more permeable foils such a limit if any was greater than 5 liters per minute. With an anodic film area of about 1 sq. cm. and flows below 5 liters per minute, this limiting rate of transport of water is about 4.3 cc. per day. At 1.2 cc. per day, saturation is reached at air flows of 0.2 liters per minute.

Foil sections with long time of extra immersion exhibited permeabilities too great for measurement. Those from the tops of completely anodized sheets and anodic film prepared by action of mercuric chloride could be measured.

Sections with extra immersion time of about 20 minutes exhibited initial rates of the order of 0.3 to 1.4 cc. per sq. cm. of foil per day. These declined with time. Upon sealing, they fell one-hundredfold.

Anodic film isolated *in situ* by the action of mercuric chloride gave very low initial rates. The rate was 0.014 cc. per sq. cm. per day when a $2\frac{1}{2}$ per cent mercuric chloride solution was used and 0.0039 when a 5 per cent solution was used.

DISCUSSION

The anodic layer consists of nearly pure aluminum oxide when formed in chromic acid but contains 10–13 per cent SO_3 and a few per cent water when prepared in sulfuric acid (6). It is amorphous to X-rays (7, 8).

Electron microscopy (9, 10), gas adsorption data (11), the dyeing of anodic film (12), and the demonstration that anodic film grows at the interface between aluminum and film and not at that between film and acid (13) all show that the bulk film is penetrated by myriads of sub-

microscopic pores. When formed in sulfuric acid these have an average diameter of about 110 Å and there are about 1.55×10^{11} per sq. cm. (11). The percentage of void is thus 14.5 if the pores are parallel and normal to the surface. It is unlikely that the error in these figures can exceed a factor of two. It is also probable that the fraction of the total volume constituted by pore space will not diverge greatly from this figure for most anodizing processes.

The degree of reproducibility of the measurements with different samples of isolated anodic film is only fair probably because the properties of the film depend upon mechanical properties slight variations in which will cause large deviations. In spite of this, a number of useful conclusions may be drawn.

Measurements on comparable sections of the same sheet generally agreed to within 20 per cent. Those on sections of different sheets of similar preparation, in some cases, diverged by a factor as great as 2. Sections isolated by the action of mercuric chloride solutions on free anodized foil gave apparently rather poor reproducibility, which one might expect because of the erratic deposition of alumina on the anodic film. Sections sealed *in situ* and treated with mercuric chloride solutions gave better results. Since the experimental work reported here covers a wide field in part only in an exploratory fashion, it is possible that further work would result in increased reproducibility.

Action of the anodizing electrolyte upon the anodic layer is clearly demonstrated by comparing permeability measurements on upper and lower sections of foil fully anodized by the rising immersion technique. Upon removing a sheet of anodized foil from the bath following such treatment, the upper parts have just been converted completely to anodic film while lower sections have been exposed to attack by the bath subsequent to complete anodization. The upper section is found to be the less permeable. The approximate value of the ratio of permeability of a section of one hundred minutes extra immersion to one of twenty-four minutes by various techniques is: Salt diffusion 10; osmosis 8; and conductance 3.5 to 5. A similar effect was found with water transport, but the rate was too fast for measurement in the more permeable cases.

The behavior of foils fully anodized in sulfuric acid and in chromic acid is surprisingly similar. By osmosis, the foils anodized in sulfuric acid are less permeable by a factor of about 3. If one takes the value of R_2 in 0.01 M or 0.1 M potassium chloride as the criterion, a similar value is found for conductance. By water transport the foils anodized in sulfuric acid seem less permeable. Owing to the fragility of the thin anodic films prepared by complete anodization in chromic acid, only one run is available for comparison with the sulfuric acid case. With one hundred and six

and one hundred and eleven minutes respectively of extra immersion, the chromic acid anodized film is the less permeable.

Data to permit comparison of anodic film anodized in chromic acid and in sulfuric acid when liberated by mercuric chloride are not available. Certain conclusions may be reached, however, in comparing films prepared by complete anodization with those isolated by mercuric chloride. Film isolated by simple action of mercuric chloride solution on anodized foil is unsuitable for investigation owing to deposition of alumina during the separation of the aluminum-anodic film interface. If but one face of anodized foil is exposed to mercuric chloride solution, that face is rapidly separated from the aluminum. The aluminum is then slowly dissolved freeing the other face in a debris free condition. Such film seems much more suitable and more reproducible. The permeability decreases with increasing concentration of mercuric chloride as judged by results with osmosis, salt diffusion, and water transport. Film isolated in $2\frac{1}{2}$ or 5 per cent mercuric chloride is much less permeable than that prepared by complete anodization. However, if one considers the permeability of film prepared by complete anodization and of zero time of extra immersion as obtained by extrapolating, the difference is reduced. Film isolated by mercuric chloride usually increased in permeability during a run. The contrary was generally true with that prepared by anodization. However, the induction period found in the osmosis experiments with sections 1 and 2 of Foil A35, which had the shortest times of extra immersion of any studied (fourteen minutes), suggests that film of zero time of extra immersion might more closely resemble that prepared in mercuric chloride solutions.

The effect of "sealing" the anodic film is striking. Exposure to boiling water for fifteen minutes reduces the permeability of the film by a factor of about 100. This is in good agreement with the well-known increase in corrosion protection afforded by sealing anodized aluminum and with the decrease in surface area as measured by gas adsorption (11). It is believed to result from the closing of pores by growth of boehmite (α-alumina monohydrate) crystals(8).

Anodic film is permeable to solute molecules in water. This is shown by results of diffusion and osmosis experiments. In particular, molecules as large as sucrose can diffuse through the film. The dyeing of anodized aluminum has long demonstrated the ready penetration of large dyestuff molecules into anodic film.

The rate of diffusion of potassium chloride through anodic film is found to be proportional to the concentration gradient in the range 0.1 M to 1.0 M. Integral diffusion constants are known to change but little in this range (14).

The nearly equal diffusion rates of a 0.1 M potassium chloride and 0.1 M potassium nitrate are in accord with the results of Clack (15) from whose data the ratio of diffusion constants at 18.5° is 1.05.

These results are important in connection with the corrosive action of solutions of halides on aluminum or anodized aluminum as contrasted, for instance, with that of potassium nitrate solutions. It is now clear that the exceptional corrosive action of the halide ion is not a result of any special case of penetration of the bulk anodic film.

Phenomena related to permeability may be divided into two groups: those in which the fluid medium itself moves, such as water transport, osmosis, and gas flow under pressure; and those in which the fluid medium is substantially stationary, such as solute diffusion and conductance by solute ions. If the film is entire pierced by its pores and if the pore volume is constant, the characteristics of the last group will be independent of pore radius. The rate of water transport will be proportional to the pore radius, while osmosis and gas flow would depend upon the square of the radius. Thus, the ordering of permeability of several films might be different by different techniques.

The quantitative comparison of rates of osmosis and water transport is of interest. Berkeley and Hartley (16) demonstrated that for copper ferrocyanide membranes the rate of osmotic flow was proportional to osmotic pressure and equal to the rate of flow under a hydraulic pressure equal to osmotic pressure over the sucrose concentration range of 0.1 to 0.3 M. The osmotic pressure of a 0.2 M solution is 4.9 atmospheres at 25°C. by the laws of dilute solutions.

If the pores in the film be assumed to increase in diameter near the surface owing to solvent action of the anodizing electrolyte, their radius may be 60 Å at the surface. Consequent to surface tension, the effective pressure impelling water into such a pore at 25° is

$$P = hdg = \frac{2\gamma}{r} = \frac{2 \times 72}{6 \times 10^{-7}} \textit{ dynes per sq. cm.}$$

if the contact angle is zero and the surface tension of water is taken as 72 ergs per sq. cm. This is 240 atmospheres. If water is evaporated rapidly enough from one end of a pore, the flow will be determined by the resistance of the pore and by the effective pressure. The ratio of the rates of flow in water transport and osmosis should then be 240/4.9 or 50.

With less permeable foils, the rate of water transport becomes independent of rate of air flow at increasing rates of air flow. In such cases it is safe to assume that the water-air interface has retreated into the pores and that the mechanism suggested above is operative. This conclusion is confirmed by considering the rate of free evaporation of water at 25° C.

This will equal the rate of condensation at a relative humidity of 100 per cent, or the rate at which water molecules at a pressure of 23.8 mm. (3.17×10^4 dynes per sq. cm.) strike unit area. In the kinetic theory of gases the following expression gives mass striking unit area in unit time:

$$mass = p\sqrt{M/(2\pi RT)}$$

This gives 0.34 g. per sq. cm. per sec. Even allowing for a diffusion film it is hard to see how the rate of evaporation can be the limiting factor.

Owing to the difficulty in measuring faster rates of flow in the water transport apparatus and to the induction period with the less permeable sections which had been completely anodized in sulfuric acid, ideal bases for comparison are not at hand. However, the rates of water transport and of osmosis on the comparable sections 1 and 3 of Foil A37 on the third day of runs were 1.2 and 0.005 cc. per sq. cm. per day, a ratio of 240. Sections from the bottom of foils completely anodized in chromic acid yield rates of osmosis of about 0.07 cc. per sq. cm. per day. The rate of water transport would be predicted to be $0.07 \times 240/4.9$ or 3.4 cc. per sq. cm. per day. Observed rates are considerably greater, being about 50 cc. per sq. cm. per day for section 3 of Foil A37.

If an osmotic membrane is not perfectly semipermeable, measured osmotic pressures are less than calculated. Since anodic film in some cases is demonstrably permeable to sucrose, rates should be lower than those computed above. Pending quantitative study of the rate of diffusion of sucrose, the rates of osmosis are not of absolute significance, but they probably are of interest in the relative ordering of anodic films.

By Poiseuille's Law,

$$V = \frac{\pi p r^{4} t}{8 l \eta},$$

one may compute rate of water transport. Considering that for anodic film anodized in sulfuric acid the pore number is about 1.55×10^{11}, r is 5.5×10^{-7}, l is 0.004 cm., p is 2.4×10^{8} dynes per sq. cm., and at 25° η is 9×10^{-3} poise; the rate of flow would be 3300 cc. per day. Granted that the calculation is sensitive to errors in r, it must be noted that the observed rate on anodic film prepared by complete anodization and of short time of extra immersion is much less than $\frac{1}{1000}$ of the computed.

If the bulk anodic film is pierced entirely by pores, one would expect the resistance of the film to equal that of the electrolyte in the pores. By the International Critical Tables, the resistivity at 25°C. of 0.1 M potassium chloride is 78 ohms cm.$^{-1}$. Whence the resistance of foil 0.004 cm. thick whose pores constitute 0.146 of the whole volume is 2 ohms. Observed resistances are at least twenty times as great.

The current view of the growth of anodic film during anodizing (17, 10, 18) is that a nonporous layer of amorphous aluminum oxide is formed by what is essentially the migration of the oxide ion lattice into the aluminum lattice occasioned by the electrical gradient of 10^7 volts cm.$^{-1}$ prevailing in this layer. The "barrier layer" upon attaining a critical thickness is pierced by electrical breakdown to form a pore from the root of which the barrier layer reforms. The thickness at which the breakdown occurs is a function of the electrolyte in a way as yet obscure. By analogy with the film formed upon anodizing in boric acid-borate solutions used in electrolytic condensers, the thickness of the barrier layer in millimicrons would numerically equal the anodizing voltage. Thus for anodizing in sulfuric acid the critical thickness would be 0.02 μ, for chromic acid 0.04 μ.

If this theory is true, at the moment the aluminum disappears during the process of complete anodization, two barrier layers are left back to back. These are then subjected to the thinning action of the anodizing electrolyte during further standing. This action is not inordinately rapid (19, 20).

In film liberated by action of mercuric chloride, the porous layer should be unchanged. The barrier layer can be penetrated by mercuric chloride (2) but when the film face is protected and the film liberated by the dissolution of aluminum from the direction of the other face, it is difficult to say just what the effect of the mercuric chloride would be. A section of film prepared by complete anodization in sulfuric acid was soaked in mercuric chloride solution and washed. Its behavior in respect to electrical characteristics was negligibly altered.

The concept of two layers, a porous and a comparatively impermeable one, is consistent with our results. The rates of diffusion and water transport indicate a considerably greater resistance than that provided by a simple pore system. The effect of continued immersion in the electrolyte is difficult to understand on pore widening alone. Thus the tenfold increase in diffusion rate shown in Table I would have required the alumina to have vanished. Rather, the increase in diffusion rate is probably connected mostly with the thinning of the barrier layer. At the roots of pores formed just before current interruption the barrier layer will be very thin, at others, at the maximum thickness. Thinning may thus cause some pores to penetrate the film completely.

The action of the film as an osmotic membrane is no doubt a consequence of the barrier layer. Since the diffusion coefficient of sucrose is one-fourth that of potassium chloride at 0.2 M (5), the rate at which it should diffuse, assuming a simple porous structure, can be computed from the measured diffusion rates. In the run with 0.3 M sucrose on Foil A2 (Table V) the foil area was 0.96 sq. cm.; the volume of the osmometer was 4.4 cc. On

the basis of the diffusion rate for section 3 of Foil A20 (Table I) the rate of loss of sucrose should have been initially 3.0×10^{-5} moles per day. The initial number of moles in the osmometer was 1.3×10^{-3}. Upon correcting for the dilution occasioned by the influx of water, the plot of flow *vs.* time declined less rapidly over a thirteen day period than one would predict on the basis of sugar loss given above. Perhaps the barrier layer is less permeable to sucrose than to salts.

Change in permeability of anodic film is probably largely related to changes in the barrier layer particularly in the first day or so. Pullen (21), however, reports that upon forty-day immersion in cold water, boehmite formation is evident. This would reduce permeability by sealing pores.

The observed magnitudes of the resistance of the anodic film, the large apparent capacitance associated with it, the frequency dependence of these properties, the non-linear dependence of resistance on the resistivity of the electrolyte, and its dependence on the measuring voltage are inconsistent with a film structure of parallel open tubes. They are, however, consistent with a structure in which a residual barrier layer constitutes the main impediment to current flow.

Since this sort of behavior seems to be in general associated with solid dielectrics (22), it is difficult to deduce specific structural details of the anodic film. However, the measured value of R_2 is proportional to the film permeability as measured in other ways. The representation of the film characteristics in terms of a parallel resistance-capacitance circuit has no absolute significance. It may be possible to represent the anodic film by a network of a sufficient number of frequency independent elements, but the interpretation of such a circuit would probably be difficult.

Any discussion of this paper will appear in the discussion section of Volume 94 of the Transactions of the Society.

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THE SITUS OF THE DEPOLARIZING REACTION IN THE DRY CELL[1]

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ABSTRACT

Measurements of pH and analyses of portions of the manganese dioxide: carbon mix show that the depolarizing reaction in the cathode of the modern cylindrical type dry cell on heavy continuous test begins in the middle and inner portions of the bobbin, i.e., those portions nearest the central carbon electrode. As discharge proceeds, the reaction (reduction of MnO_2) spreads to include the remainder of the cathode, the outer portions being reduced to a greater extent than the rest of the bobbin.

INTRODUCTION

Much attention has been given, particularly in recent years, to the cathodic processes during dry cell discharge (1, 2, 3, 4), and a reasonably clear picture of the chemical and electrochemical reactions involved is gradually developing. On the other hand, surprisingly little has been published on an equally important subject, the situs of the cathodic reaction: where it begins and how it proceeds.

Attempts at mathematical solution of the problem of reaction situs have been made, but in these the cathode has usually been considered on a purely physical basis, without due regard to such variables as electrolyte pH and composition, depolarizer potential, or changes brought about by diffusion processes. The widely held view that depolarization begins at the outer surface of the bobbin of the cylindrical type cell and proceeds toward the central electrode soon encounters difficulty and is hard to reconcile with actual resistance measurements (4), diffusion data, and other characteristics of cell discharge.

We are aware of the efforts to determine the progress of the cathodic reaction[2] with resistance or potential measurements made by means of exploring electrodes, usually of platinum or carbon, placed at various distances between the central carbon rod and the periphery of the bobbin, and we ourselves have made many measurements of this nature. Such electrodes contact the carbon of the depolarizer mix and, therefore, the resistance measurements reflect changes in the solid phase which generally throw little light on the discharge mechanism. Potential measurements

[1] Manuscript received July 4, 1948. This paper prepared for delivery before the New York Meeting, October 13 to 16, 1948.

[2] The most recent of these is included in a mathematical study of the relation between ampere-hour capacity and drain, by J. J. Coleman (5).

made between pairs of such exploring electrodes are also of doubtful significance, being complicated during closed circuit by IR drop and during open circuit by contact with the continuous carbon phase which tends to equalize any potential differences between various parts of the cathode. Fortunately there is an easily determined factor, the rise in pH, which is directly related to the cathodic reaction, at least during the initial portion of the dry cell discharge. The significance of this factor, based on progressive pH measurements at selected points within the cell, together with supporting analytical data, furnish the basis for this paper.

EXPERIMENTAL

D size general purpose type flashlight cells[3] (6) were placed on 4 ohm continuous test (7) at 21°C. Periodically, representative cells were taken off test and opened, the carbon electrodes were removed, and the central portions of the mix bobbins were quickly withdrawn by means of a chro-

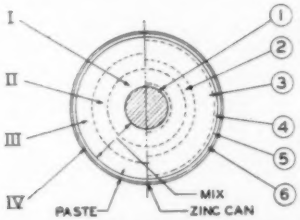

FIG. 1. Cell cross-section, showing location of samples for the pH measurements in Fig. 2 (Roman numerals) and Fig. 3 (Arabic).

mium plated cork borer $\frac{1}{2}$ inch (1.27 cm.) diameter. A second sample, concentric with the first, was then taken from each cell in the same way, using a $\frac{3}{4}$ inch (1.90 cm.) diameter cork borer. The remainder of the mix was then removed from the surface of the adhering paste layer. The innermost, middle, and outer samples of cathode mix thus obtained weighed approximately 9, 22, and 13 grams respectively. Measurements of pH were made on the thoroughly mixed combined portions from duplicate cells and a part of each sample so prepared was dried in a vacuum at 80°C. in preparation for analysis by conventional methods. The pH of a representative sample of the paste portion of the cell was also measured. The locations in the cell from which the samples were removed are shown in Fig. 1 (indicated by Roman numerals), and the data obtained are presented in Fig. 2 and Table I.

[3] The cells contained the following active ingredients:

Depolarizer (African MnO_2 ore)	24.9 g.
Zinc chloride ($ZnCl_2$)	1.25 g.
Ammonium chloride (NH_4Cl)	7.42 g.
Water	10.85 g.

In similar tests, duplicate cells were opened by splitting zinc can and bobbin lengthwise, and samples representative of thinner mix layers were taken from the locations indicated by the Arabic numerals in Fig. 1. The

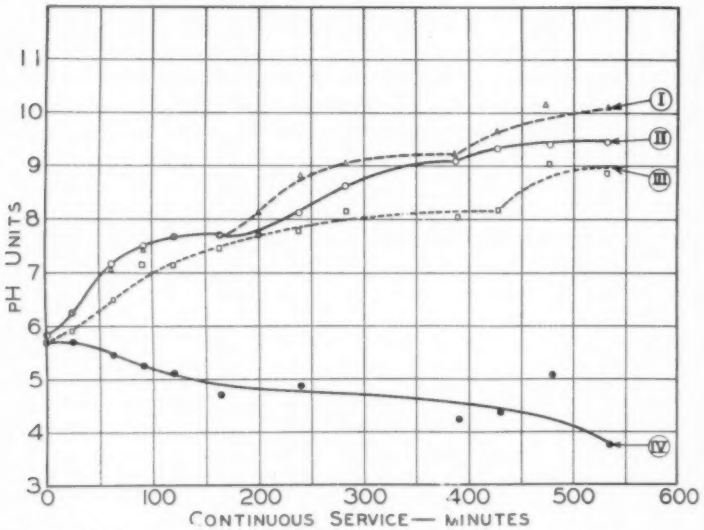

FIG. 2. pH changes during dry cell discharge. (Locations of samples taken for pH measurement—designated by Roman numerals—are shown in Fig. 1.)

TABLE I. *Reduction of available MnO_2 at three locations in the cathode*

Service on 4 ohm continuous test	Utilization of available MnO_2		
	Innermost layer	Middle layer	Outer layer
min.	*per cent*	*per cent*	*per cent*
0	0	0	0
25	1.21	3.56	0
63	3.39	3.56	6.86
92	6.78	7.13	7.87
121	8.71	11.40	14.74
165	9.68	—	15.23
240	15.00	17.10	20.41
285	16.46	17.32	23.76
390	23.20	23.66	30.03
480	24.20	30.60	36.00
540	28.50	31.58	37.05

sample designated by No. 3 represents the layer just underneath the hardened outer crust of mix formed during the intermediate stages (150–350 minutes) of continuous discharge (4). It will be noted that two paste

samples were also taken, one No. 5, next to the bobbin surface, and the other, No. 6, next to the zinc anode. The data obtained are presented in Fig. 3.

The pH measurements were made with a glass electrode, Leeds and Northrup No. 1198–8, using a potentiometer-electrometer Leeds and Northrup No. 7660-S and the usual accessory equipment. The apparatus was calibrated immediately before use in a series of standard buffer solutions obtained from the LaMotte Chemical Products Company of Balti-

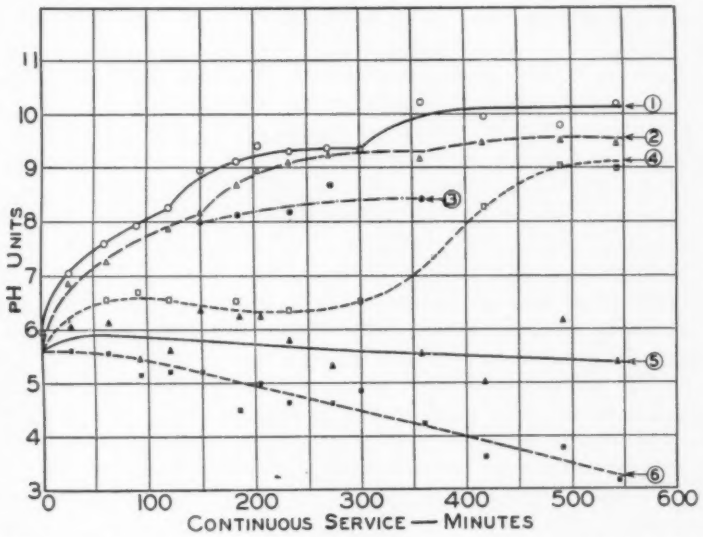

Fig. 3. pH changes during dry cell discharge (samples, representative of thin sections, taken from locations indicated by Arabic numerals in Fig. 1.)

more, Maryland. Although no extreme accuracy is claimed, the only known sources of error are those due to the presence of the solid matter of the mix which limits the quantity of electrolyte in contact with the glass electrode, and to the loss of ammonia during sampling and pH measurement. Neither of these errors is believed to be great enough to affect the significance of the readings obtained.

DISCUSSION

This paper represents an extension of the technique, introduced in a previous contribution from this Laboratory (4) for studying the reactions in a dry cell during 4 ohm continuous test at 21°C. The cells used were

the same as those previously described and showed identical discharge characteristics.

For cells of this type, the predominant cathode reaction,

$$2MnO_2 + 2NH_4^+ + 2e \rightarrow Mn_2O_3 \cdot H_2O + 2NH_3$$

means a rise in mix pH as reaction proceeds.[4] Therefore, at least in the early stages of the dry cell discharge, the location at which the pH has risen most indicates the situs of the greatest amount of cathodic reaction. As applied to the curves in Figures 2 and 3, this means that initially the cathode reaction proceeded most rapidly in those portions of the bobbin near the carbon electrode.[5] The pH data, in conjunction with the analytical results in Table I, would appear effectively to dispose of the idea that the reaction originates in the outside layers of the cathode.

The course of the pH curves has a number of points of interest. Quite obviously pH does not determine the reaction situs in the later stages of cell discharge since the greatest amount of MnO_2 reduction occurs at the outer portion of the bobbin and is accompanied by the smallest rise in pH. In this case, obviously, the rise in pH has been reduced by diffusion of acidic, anodically formed $ZnCl_2$ into the bobbin.

The inflection points in the curves for the cathode samples of Fig. 2 and 3 correspond to stages of neutralization of $ZnCl_2$ and the formation of polyammino compounds, such as $ZnCl_2 4NH_3$ at pH 8 and a second complex of the type $ZnCl_2 8NH_3$ at the higher pH 9.2 level. The location of the first points of inflection (pH 8) in Fig. 2, Curves I and II, occurs 35 to 60 minutes later than would be expected from the initial cathode composition, this difference being accounted for by diffusion of $ZnCl_2$ from the paste layer. When a very thin mix layer at the carbon electrode is examined, as in Curve 1 of Fig. 3, the first inflection point occurs about 20 minutes earlier than expected from the initial cathode composition, showing a concentration of cathodic reaction in this portion of the bobbin.

Further evidence on the process of diffusion of $ZnCl_2$ from paste to mix during test is given by Curves 3 and 4 of Fig. 3. As previously (4) established, the outer layer of mix becomes hardened to a depth of about $\frac{1}{64} - \frac{1}{32}$ inch, (0.4–0.8 mm.), by precipitation of neutralization products, e.g., $ZnCl_2 \cdot 2NH_3$, during a part of the test, in this particular series of cells in the period from 150 to 350 minutes. The samples taken for Curve 4 consisted mainly of this layer and it is not surprising that during the period

[4] The formation of Hetaerolite (3) obviously would not involve a similar change in pH but, for the experimental conditions chosen, this reaction is of negligible proportions and may be ignored.

[5] Coleman (5) states (page 558): "Thus at the beginning of the discharge when the e.m.f. is the same thruout the bobbin, one would expect to find the current strongest through the particles near the carbon rod and near the edge of the bobbin."

of precipitation the pH should not materially change. However, after about 350 minutes service the concentration of NH_3 had increased sufficiently to redissolve the precipitation product, the hard layer disappeared, and the pH in Curve 4 rose accordingly. Curve 3 of Fig. 3 shows the pH values of the mix adjacent to the hardened layer described with values not greatly different from those of Curve III, Fig. 2, i.e., for larger samples taken from the same general location.

The pH development in the paste layer shows the effect of the accumulation of $ZnCl_2$ in this portion of the cell. By the time the test is completed, the concentration of $ZnCl_2$ developed at the anode surface, judged from the pH data (Curve 6 of Fig. 3), amounts to 42 per cent, a value confirmed by other measurements.

It must be emphasized that the investigations presented here cover only a very limited set of experimental variables and test conditions and that, with different testing schedules and cell compositions, values varying considerably from those reported may be obtained. On lighter drain tests, for example, a smaller pH range is recorded.

The pH data presented definitely indicate that the situs of the dry cell cathodic reaction at the beginning of 4 ohm discharge is in the central portion of the depolarizer mix. These findings are confirmed by analytical data. As discharge proceeds the analytical data indicate an increasing proportion of the reaction in the middle and outer layers of the bobbin, although this is not suggested by the pH curves. This apparent anomaly, and the general mechanism of the cathode reaction in the later stages of the dry cell discharge are being investigated further.

Any discussion of this paper will appear in the discussion section of Volume 94 of the Transactions of the Society.

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TWENTY-FIVE YEARS' DEVELOPMENT OF THE SÖDERBERG SYSTEM IN ALUMINUM FURNACES[1]

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ABSTRACT

It is now twenty-five years since the Söderberg Electrode was first used in commercial aluminum furnaces, and this article is a review of the developments which have taken place during these years, and the difficulties which have gradually been overcome. The new type of electrodes with vertical contact studs provided with direct collection of the furnace gas and a gas burner, which are described, have given excellent results in large furnaces of 60,000 amp. or more, and combine the advantages of both open and closed furnaces.

INTRODUCTION

The first Söderberg electrode to be used in a commercial aluminum furnace was started in the year 1923 in the Norwegian aluminum works of A/S Vigelands Brug, a subsidiary of The British Aluminium Company. Preliminary tests had previously been carried out by Elektrokemisk at Fiskaa Verk, and also at Vigeland.

It therefore seems opportune to review the developments which have taken place in this field during the last twenty-five years—developments which have resulted in the installation of the Söderberg electrode system in aluminum furnaces, with a total capacity of approximately 1,000,000 tons of aluminum per year, about half of which are installed in America.

As an illustration of the remarkable advances made in the aluminum industry during these past twenty-five years, it is interesting to contrast the first furnace of 8,000 amp., producing approximately 50 kg. of aluminum per day, with the large units of the present, the rating of which has in many cases been increased to 60,000 amp. and even considerably more. Whereas the furnaces of 1923 required about 24,000 kw.-hr. per metric ton of aluminum, with an electrode consumption of about 700 kg. per ton, including electrode butts, aluminum is produced in the modern large Söderberg furnaces using only 15,500 kw.-hr. and approximately 500 kg. electrode paste per ton.

EARLY TESTS

The Söderberg electrodes in the smelting industry have remained fundamentally unchanged since they were first demonstrated to an inter-

[1] Manuscript received July 15, 1948. This paper prepared for delivery before the New York Meeting, October 13 to 16, 1948.

national committee in 1919 (where the U. S. A. was represented by Dr. J. W. Richards). In aluminum furnaces, however, a long series of developments have been necessary in order to arrive at good practice, in spite of the inherent advantage of the Söderberg system in that it is the only continuous electrode which has been brought into commercial use in such furnaces. The main reason for the many difficulties encountered was that the first Söderberg electrodes were provided with iron ribs (1) for the purpose of conveying the electric current to the baked part of the electrode and securing a good mechanical connection between the suspension device and the electrode. These ribs, when used in aluminum furnaces, introduced considerable amounts of iron into the metal and it, therefore, proved necessary to make radical changes in order to obtain satisfactory results.

The first Söderberg electrode at Vigeland in 1923 was provided with an aluminum casing with iron ribs (aluminum ribs cannot be used, as they would melt before the electrode could be sufficiently baked). The iron ribs were reduced in size and made only 0.1 mm. thick. It was thereby possible to reduce the amount of iron introduced into the aluminum through the ribs to approximately 0.1 per cent, which did not seem too serious at that time. The possibility of arriving at a continuous electrode of practically unlimited size seemed very tempting to most aluminum plants, and trial installations were built in aluminum furnaces at works in Germany, France, Switzerland, and the United States, the last-mentioned being of 16,000 amp. at Badin, North Carolina.

During the next few years a number of tests were carried out in these different trial installations. However, it was found necessary to make a slight increase in the amount of iron in the ribs, as the voltage drop in the anode would otherwise be too high. Even when 0.18 per cent Fe was introduced into the metal, the anodic voltage drop measured about 0.7 volts, as against the 0.3–0.5 volts in the pre-baked electrodes. These tests, therefore, placed the research staff in a constant dilemma: either too much iron would be introduced into the aluminum, or the voltage drop in the electrode would be too high. It became increasingly necessary to compromise in one way or another, although such a compromise could never be quite satisfactory, either as to introducing impurities or as to the voltage drop in the anode.

During these years the aluminum industry had steadily improved operations, and particularly in respect to the purity of the metal which was standardized at 99.5 per cent Al. It was found, however, that the metal produced by means of these trial Söderberg electrodes tended to be off-grade when compared with the metal produced with pre-baked electrodes, at least if the voltage drop was to be the same. One by one, the trial furnaces were shut down, and it became even more urgent to find a better way of conducting the electric current to the electrode.

INTRODUCTION OF INDIVIDUAL CONTACT STUDS

A great number of tests were at that time being carried out at Elektrokemisk's research plant, and in 1925 the individual contact studs were developed. These studs were introduced into the upper unbaked part of the electrode from the side. In the course of their downward movement, the studs were gradually baked into the electrode through the coking of the binder on their surface. The studs were removed by extraction before they came into contact with the cryolite bath in the furnace (2). This method gave an excellent contact between the studs and the electrode,

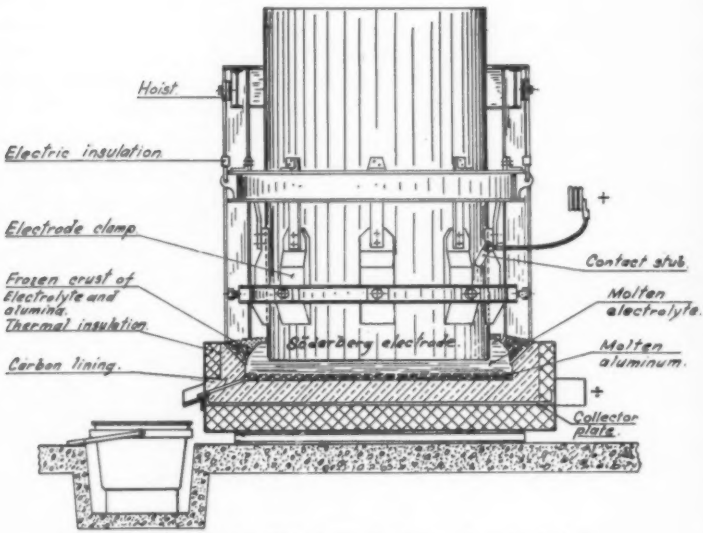

FIG. 1. Circular Söderberg electrode of early design

so that a very satisfactory voltage drop was arrived at and, at the same time, the introduction of iron into the metal was avoided. It proved possible to introduce the electric current into the baked part of the electrode without danger of contaminating the metal. The purity of aluminum produced with Söderberg electrodes became even superior to that produced in furnaces equipped with pre-baked electrodes.

The trial installations still existing at that time in Norway, France, and the United States were rapidly adapted to the new system, and the results looked very promising. A commercial plant was installed in France and also, in 1927, in Spain, followed by another in Alcoa, U. S. A. These plants used 11,000, 14,000 and 30,000 amp. respectively. On the basis of

this system a race began between the Söderberg furnaces and the furnaces using pre-baked electrodes. This race which has been going on ever since has been both interesting and exciting. The Söderberg furnaces often seemed to be gaining the upper hand, but the pre-baked carbon furnaces also proved capable of improvements and, even now, the question as to which system is the most efficient has not been finally decided. No doubt, this competition has materially contributed to the development of the aluminum industry.

RECTANGULAR ELECTRODES

Up to about 1930, the Söderberg electrodes, and the aluminum furnaces in which they were installed, were of circular cross section. In the initial stages the electrodes were suspended by means of a gripping holder, the design of which was based on the electrode holders used with Söderberg electrodes for smelting furnaces (3). Another interesting solution which was developed in France was also adopted with considerable success in other countries (4). During this period the amperage of aluminum furnaces was increased little by little until, at the end of the twenties, 30,000 amp. furnaces were erected. These large furnaces required Söderberg anodes of approximately 2.25 m. diameter, and it was found necessary to reduce the current density on the anode as compared with smaller furnaces, so that approximately 0.7 amp. per cm.^{2} was used for 28,000 amp. In comparison, the furnaces with pre-baked electrodes ordinarily used about 1 amp./cm.^{2} In small Söderberg furnaces with electrodes of approximately 1 m. diameter an amperage of 0.9–1.0 amp./cm.^{2} was used successfully.

The reason for reducing the ampere density on the big anodes has never quite been explained. It may have something to do with the longer path of escape of the gas developed underneath the anodes. The gas forms bubbles which, in escaping, cause movement (waves) in the metal surface on the bottom of the furnace. This movement is probably stronger the larger the bubbles and the longer the passage of the gas. The height of the waves on the metal surface determines the minimum distance between anode and cathode and thereby also the voltage of the furnace. In order to obtain a good ampere efficiency when using big anodes, the current density should be reduced so as to allow the waves to quiet down. If the current density is not reduced, it is necessary to increase the distance between anode and cathode whereby the voltage drop is raised and overheating may result. However, the larger the diameter of the anode, the higher and also the heavier the anode will be, which of course causes an increase of installation costs.

As the operating results of the big circular Söderberg furnaces were not

sufficiently good to compete with the improved furnaces operating with pre-baked electrodes which came into use at that time, rectangular Söderberg electrodes were tried in the United States as well as in France. The French installations (5) (Cie. Alais, Froges et Camargue) were so successful that a commercial series of 22,000 amp. furnaces with rectangular electrodes was put into operation in 1931.

The suspension of the rectangular anodes consisted of steel frame sections mounted around the electrode as it was lengthened, but removed from the same before they touched the cryolite bath. The contact studs were inserted through holes in the frame. Later on, another type of suspension was developed, consisting of a permanent iron casing surrounding the electrode, through which the electrode could be slipped into the

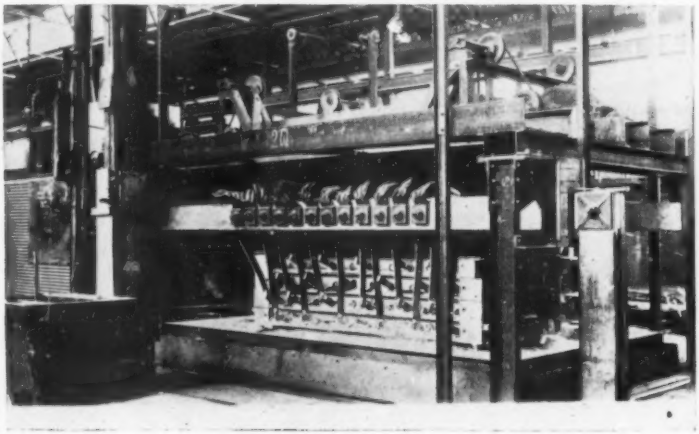

FIG. 2. Open type furnace of 23,000 amp.

furnace as the lower end was consumed. In order to permit introduction of the individual studs from the outside, the casing was provided with slots, the length of which corresponded to the traveling distance of the studs from their upper position to the lower. At their latter position the studs were just above the level of the cryolite bath and had to be removed by extraction. Both these methods of suspension are in commercial use today.

CLOSED FURNACES

The furnaces described above showed another novelty which was successfully developed and demonstrated and was found a great deal of interest in the aluminum industry. They were closed (6) and connected to a system for gas collection and purification.

A detailed account of this interesting furnace type has been published previously (7). It was a great disadvantage in the aluminum industry that the fumes and gases developed during the process had been allowed to escape freely in the furnace room. These gases contain fluorine and carbon monoxide and, in addition, fumes are also developed by the Söderberg electrodes during the baking process. All this caused considerable discomfort in the furnace room, while the harmful effects of the escaping fluorine gases on the surrounding vegetation and animal life are well known. The gas cleaning question had, therefore, been a serious problem for many aluminum plants for a long time and several plants had been involved in lawsuits in this connection. These new closed furnaces proved for the first time that it is possible to collect the gas and clean it, so as to eliminate the harmful effects of aluminum plants on their surroundings.

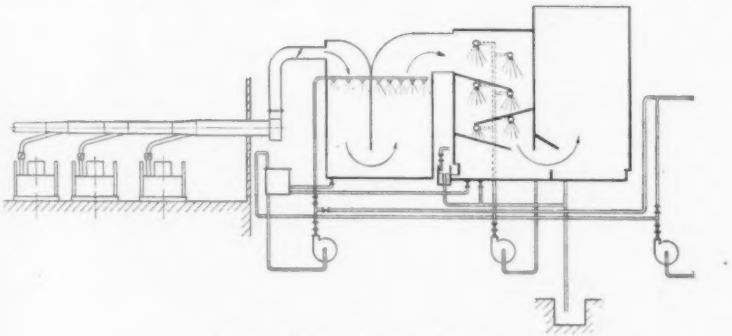

FIG. 3. Wet gas cleaning system

They, therefore, constitute a decided and important advance in the aluminum industry, and were quickly adopted by a great many plants all over the world. Installations were made in Germany, Great Britain, Hungary, Italy, Japan, Norway, Sweden, Switzerland, and Yugoslavia, as well as in Canada and in the United States.

The gas cleaning, as developed by Cie. Alais, Froges et Camargue, Paris, consists of scrubbing the gas with a solution of Na_2CO_3, thereby producing NaF. This solution is recirculated until it has reached a concentration sufficiently high for use in the production of artificial cryolite, subsequently to be used in the electrolytic furnace. A substantial part of the lost fluorine is thereby returned to the furnace.

By the beginning of World War II, the rectangular Söderberg electrodes and the closed furnaces had been adopted by most aluminum producing countries. During the war a number of new installations were made in many parts of the world, and the United States also adopted rectangular Söderberg electrodes in several new plants.

DEVELOPING THE SÖDERBERG ELECTRODE WITH VERTICAL CONTACT STUDS

All the electrodes hitherto described have been provided with contact studs introduced into the side of the electrode, but tests had been carried out by Elektrokemisk as early as 1919 with vertical screw contacts. These were unscrewed intermittently as the electrode was consumed at the lower end. Later on similar tests were also made in a German aluminum plant. However, it had been found that the contact screws did not stand up satisfactorily, neither was the electric contact obtained good enough. A certain voltage drop existed between the surface of the contact screws and

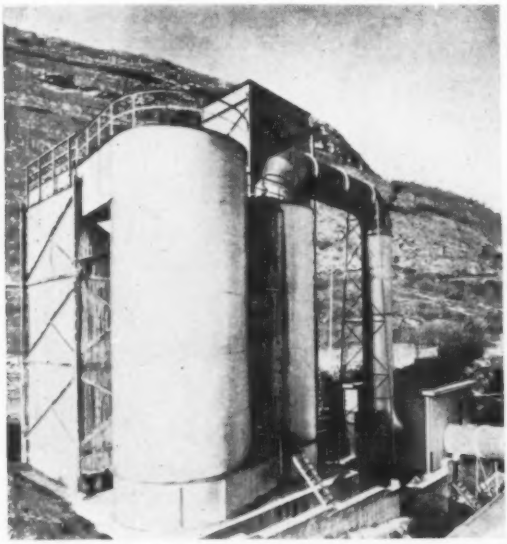

FIG. 4. Gas cleaning plant of an Italian aluminum works

the electrode proper, causing overheating of the contact by the passage of the electric current. It was quite clear, however, that the vertical arrangement of the contact screws had one important advantage: the iron casing surrounding the electrode could be made entirely closed, with no moving parts, so that the electrode could be very efficiently guided and protected down to the surface of the cryolite bath.

Montecatini in Italy put a great deal of work into the development of the Söderberg electrode with special screw contacts. This system, which was also tried for a couple of years in Switzerland, was based on the use of conical contact screws, the largest diameter being at the lower end. In

this way, a good contact was obtained even though the screws were not "coked" into the electrode (8). When unscrewed intermittently these screws forced their way through the electrode under heavy pressure. The procedure gave improved contact, but the electrode had a tendency to crack and the contacts still did not stand up satisfactorily. The system was given up after a couple of years' trial and the vertical contact studs did not find successful application until the basic principle of the individual

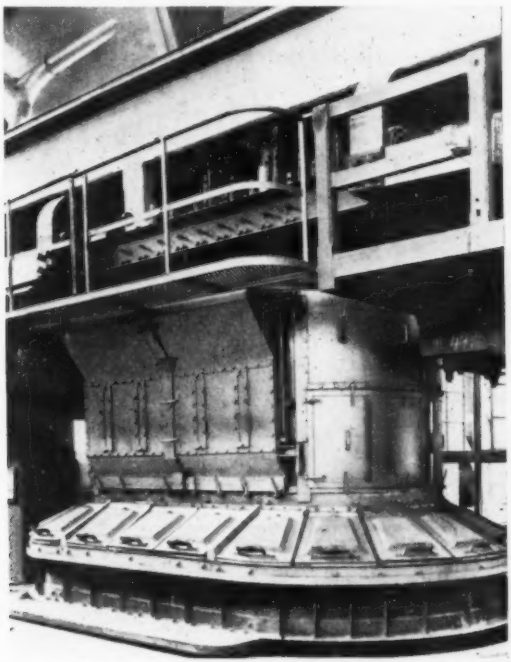

FIG. 5. Closed furnace of the Montecatini type

contact studs was introduced, i.e., the contact between the studs and baked carbon was effected by the coking of the stud surface into the electrode. A modified Montecatini type furnace using vertical conical studs of this type was installed in Mori (9), and one series of same was later on put up in Bolzano.

The system worked satisfactorily and is still being employed successfully in Bolzano. However, the installation costs were very high, in fact about twice as high as those of the other types described above. It was, therefore, obvious that simplifications would have to be made.

SIMPLIFIED ARRANGEMENT AND DIRECT GAS COLLECTION

Tests were being contemplated at the beginning of World War II in order to arrive at a simplified arrangement. Elektrokemisk then took over an idea from Mr. Bruno Luzzatto who had previously been connected with the Montecatini Works and who had been active with vertical screw furnaces in Italy and Switzerland. Mr. Luzzatto called attention to the fact that the gas from the aluminum furnace is developed at the lower end of the electrode and suggested that this gas could be collected by providing a narrow collecting channel at the lower end of the permanent casing of the electrode above the surface of the cryolite bath.

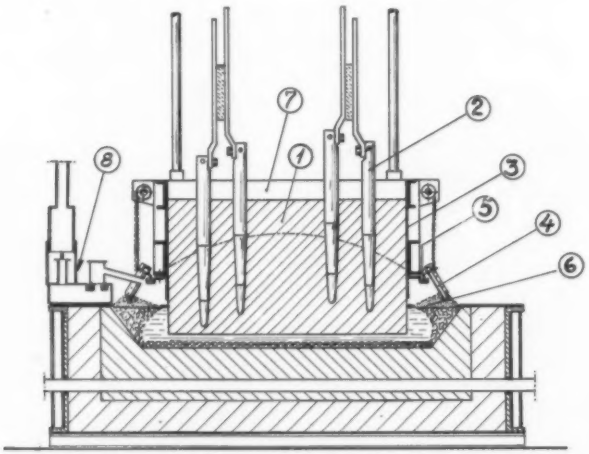

FIG. 6. Section through furnace equipped with Söderberg electrode with vertical studs.

The rights to the idea of Luzzatto were taken over in 1939 by Elektrokemisk but the outbreak of war prevented them from executing the proposed tests and work could not be continued until Norway was liberated from the occupation of the Germans. In the meantime, however, the French engineer, Mr. Robert Jouannet, of Cie. Alais, Froges et Camargue, had independently conceived the same idea as Mr. Luzzatto, and Camargue tried out the arrangement at the La Praz aluminum works. The rights of Mr. Jouannet's patent were also taken over by Elektrokemisk.

In carrying out the proposed idea, the channel at the lower end of the permanent casing of the electrode is closed by a cover which is made gastight by means of alumina and the concentrated gas may thereby be collected without the addition of diluent air. The tar content of the fumes

is destroyed by combustion of the gas in a gas burner where the CO is also oxidized to CO_2. The gas is subsequently passed through a gas cleaning and scrubbing system for collection of dust and fluorine constituents.

Mr. Jouannet also simplified the equipment and materially reduced the number of contact studs needed by adopting the practice of pulling the studs from their lower position, and immediately inserting them into the baked part of the electrode, into which they were baked by the introduction of a small amount of electrode paste into the hole containing the stud. In this way, no studs were left for any length of time in an unbaked portion of the electrode and they all contributed in conducting electric current to the electrode. The number of studs could be reduced to roughly one half of those used in Bolzano, where the studs were embedded in the upper soft part of the paste and left there to bake slowly with the paste as they approached the level of the bath.

ELECTRODES WITH VERTICAL STUDS

The sketch shows a cross-section of an electrode with vertical studs. (1) is the electrode, and (2) the studs, which are usually arranged at two or three different levels, so that $\frac{1}{2}$ to $\frac{1}{3}$ of the studs are always kept in the lowest position. As the electrode is consumed, the studs will move closer to the bottom of the electrode, and have to be pulled out and reinserted as described above.

The dotted line across the electrode shows the approximate baking zone and, as will be understood, the studs are inserted down into the lower baked part of the electrode, so that they can at once take over the current transmission.

(3) is the permanent casing surrounding the electrode. This casing serves as a container for the paste and also shapes the electrode. It will be noted that the vertical stud type electrode does not require an aluminum sheet casing, as was earlier the case.

The lower part of the electrode is surrounded by a cover (4) resting on the crust (6). This cover may be moved out of position by lifting and is sealed with alumina at the top (5) and bottom. A gas-tight channel surrounding the lower part of the electrode is thereby obtained, in which collect the gases developed by the reduction of alumina, and also tar fumes escaping from the electrode. These concentrated gases are easily ignited, and tar and CO may be disposed of in a gas burner (8).

Even after combustion, the total gas volume is rather small, amounting to 5 to 10 per cent of the gas volume collected by the previous method, and a larger gas cleaning system is, therefore, not necessary. Furthermore, as the tar fumes have already been removed, the whole question of gas cleaning and recovery of cryolite has been simplified.

Owing to the gas-tight channel surrounding the lower part of the electrode this will not be exposed to air. Air oxidation of the red-hot part of the electrode is thereby reduced to a minimum, and the total consumption of electrode is correspondingly decreased.

When charging alumina, the cover (4) is raised, and the crust (6) broken in the usual manner. After the process is completed, the cover is replaced. In this way, the furnace is operated exactly as an open furnace, and combines the advantages of the open and the closed type of furnace.

The method of reinserting the studs into the electrode has been described above. By introducing the studs into the baked part of the electrode all the studs will participate in conducting the electric current, and a low voltage drop is thereby obtained. This also follows from the fact that the end of the studs may now reach down into the electrode below the bath level.

As the vertical studs may be evenly distributed in the electrode, it is easy to obtain an equal current distribution in the different sections of the electrode, permitting the use of larger electrode sections. The suspension of large electrodes is simplified by the fact that the studs may be suspended direct from the main bus bars mounted above the electrode.

Both these factors help make it possible to install electrodes of sizes which have previously been thought impossible. 40,000, 50,000 and 60,000 amp. electrodes are now in operation, and 100,000 amp. electrodes have also been tried out. These large electrodes require a large permanent casing, and it has been found advantageous if the electrode is of rectangular cross-section, to connect the opposite sides of the casing by means of partition sheets (7) arranged in the upper part of the electrode, thereby strengthening the structure. These walls will form a "crack" in the electrode, which facilitates the escape of the gas developed underneath the electrode.

It has been extremely interesting to see how closely this new type of electrode has been studied by different aluminum companies. Lines of 40,000, 50,000 and 100,000 amp. are at present being designed, and many are actually under erection.

RESULTS WHICH MAY BE OBTAINED IN THESE LARGE MODERN FURNACES

It has been mentioned in the beginning of this article that the energy consumption per ton of metal produced has been greatly reduced in these last twenty-five years. The power consumption is naturally one of the deciding factors determining the cost of aluminum and the results of some theoretical considerations may, therefore, be of interest.

The electrochemical reactions taking place in an aluminum furnace are endothermic. The heat of reaction depends to some extent on the composition of the anode gas. Assuming a composition of 65 per cent CO_2 and 35

per cent CO, the heat of reaction corresponds to an energy consumption of 5940 kw.-hr. per metric ton of metal. The process is carried out at 950°C., and the heat content of produced metal and gasses must be added. This addition amounts to 730 kw.-hr., making the total theoretical energy consumption 6670 kw.-hr. per metric ton metal. When comparing the 25,000 kw.-hr. consumed in the early days with the 15,000 kw.-hr. per metric ton now visualized in the modern units, it will be seen that the energy efficiency is raised from about 27 per cent to about 45 per cent. Now 15,000 kw.-hr./t is still rare and, under ordinary conditions, 17–18,000 kw.hr./t is considered a good result. However, even 45 per cent energy efficiency seems rather low and this figure might be improved. Unfortunately, it is only possible to a limited degree to reduce the energy consumption by increasing the heat insulation of the furnace, which would permit the working with a smaller anode-to-cathode distance and a lower voltage drop.

However, if the above-mentioned distance is reduced below a certain minimum, the ampere efficiency will suffer. A further reduction of the voltage drop can, therefore, only be obtained by a reduction of the current density on the electrode; that is the dimensions of the furnace must be increased. The large modern furnaces with low current density have been operated on approximately 4 volts and it is expected that this figure can be even further reduced. Assuming 90 per cent current efficiency and 3.5 volts, it is possible to obtain an energy efficiency of 55 per cent.

Such an efficiency is, of course, still in the future and whether it will be obtained or not depends on the installation costs involved. This review may perhaps contribute to some extent to the furthering of the developments which are still to come and which, in due time, will give the answer.

Any discussion of this paper will appear in the discussion section of Volume 94 of the Transactions of the Society.

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COMMERCIAL PRODUCTION OF ELECTROLYTIC MANGANESE[1]

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ABSTRACT

Electrolytic manganese, 99.9+ per cent, was started in commercial production in the United States in 1939. To date, more than 20 million pounds have been produced and sold. The manufacture of the material by electrowinning in a two-compartment cell with a sulfate electrolyte is described; the properties of the pure metal are given. The applications are in nonferrous metallurgy of aluminum, copper, magnesium, zinc, brasses, and bronzes; in ferrous metallurgy of steel and stainless steel; in electrical resistance and special purpose alloys, and the manufacture of pure chemicals.

INTRODUCTION

Manganese is a very hard, grayish-white metal. In a pure state as electrolytic manganese, it scratches glass. Manganese was first isolated in 1774 by Gahn working with Scheele.

Electrolytic manganese is a growing industry and over 20 million pounds have been produced and consumed. During the war period, appreciable quantities were furnished for military needs and those of our Allies, as well as to the United States Mint for the coinage alloy of the five cent piece when nickel was displaced in coinage.

Electrolytic manganese is typically an entirely American development although some small German development and production have been reported, as well as small-scale Japanese production during World War II. The foreign plants operated only for a short period on short deposition cycles.

The production of electrolytic manganese in the United States is given in Table I, while the product is pictured in Fig. 1.

High-purity (99.9+ per cent) electromanganese, made by the electrolytic process, has firmly established its advantages by wide use over a number of years. Absence of impurities has given the nonferrous and ferrous metallurgists an alloying element which not only secures uniform results, but also in many instances has produced improved mechanical properties. Manganese metal of this purity has further made possible the development of a number of new high-manganese alloys, as well as an entirely new field of manganese-base alloys.

Manganese is used either as a scavenging agent or as an alloying element

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TABLE I. *Production of electrolytic manganese in the United States, 1939–1947, by producers, in pounds*

Year	Electro Manganese Corporation	Bureau of Mines	Total
1939	43,669	—	43,669
940	418,837	—	418,837
1941	1,190,042	—	1,190,042
1942	1,306,310	149,380	1,455,690
1943	2,385,486	464,690	2,850,176
1944	3,308,071	476,200	3,784,271
1945	3,398,569	280,336	3,678,905
1946	2,120,943	127,614	2,248,557
1947	3,499,181	—	3,499,181
1948 (6 months)	1,966,571	—	1,966,571
	19,637,679	1,498,220	21,135,899

FIG. 1. Commercial electrolytic manganese

in more alloy combinations probably than any other element. The principal combinations are those having iron, copper, aluminum, magnesium, nickel, or zinc as base metals.

The availability of high-purity electromanganese has made it desirable to review the many applications for manganese metal and has made possible

the development of numerous new high-manganese and manganese-base alloys.

Manganese is an important constituent in alloys of aluminum, copper, iron, magnesium, and zinc, as well as more complex systems involving these metals. Manganese additions to brasses, bronzes, and nickel silvers have received considerable attention. Manganese finds wide application as a scavenger, deoxidizer, and degasifier in specialty alloys for high-temperature service as those of nickel-chromium and nickel-chromium-iron, in strip steels, and a wide variety of stainless steels and irons of the manganese-chromium-iron, the manganese-chromium-nickel-iron, and other alloys. Manganese enters the field of powder metallurgy as a constituent of contacts, preformed catalysts, and sintered alloys. Its pure form makes it an ideal starting point for special chemicals of high purity.

The binary alloy systems of manganese which have been studied cover a wide range, but much of the work was done with impure manganese before the availability of pure electromanganese.

To date, no application has been developed for the pure metal alone owing to its inherent brittleness. This is probably caused by the complex allotropic forms of manganese, although it can be transformed to a ductile alloy by the addition of 2 per cent copper and 1 per cent nickel.

Electromanganese chip is readily washed into most base metals and alloys. Agitation of the bath improves both the solution rate and distribution, but for certain applications or small crucible additions it may be more desirable to use the lower melting point hardeners.

Kroll (1) holds that pure manganese which has been melted under an argon atmosphere can be hot worked in the gamma and most of the beta regions. Quenching of this pure material does not prevent transformation to the brittle alpha form. Alloying with 15 per cent of copper lowers the plastic range to 500°C., while an alloy with 5.1 per cent copper and 8.9 per cent nickel can be kept plastic and not embrittle at room temperature.

Ductile alloys may be made from electromanganese (2) by alloying with oxide-free aluminum 0.1 to 5 per cent, nickel from 2 to 10 per cent, and copper 3 to 16 per cent.

Cold workable alloys (3) have been proposed of at least 50 per cent pure manganese with 0.1 to 10 per cent aluminum, 0.5 to 10 per cent nickel, and 1 to 35 per cent copper.

MANUFACTURE

Electrolytic manganese is the product of an electrowinning operation. Manganese ores, if not already acid soluble, are conditioned by reduction procedures. Their manganese values are extracted by a sulfuric acid leaching solution, which is an anolyte from the electrolytic cells. The leach

solution, after increase in manganese content and decrease in acid, is carefully purified, and after adjustment becomes the feed liquor to the deposition cell where insoluble anodes are employed. The feed liquor enters the catholyte chamber of a two-compartment diaphragm cell where the manganese content of the feed is stripped, the solution passing through the diaphragm to become part of the anolyte. Anolyte returns in circuit to leach fresh conditioned ore and the cycle is thus continuous.

Following the early work of the United States Bureau of Mines carried on in pilot plants using domestic ores, a translation to a commercial plant was attempted. Unfortunately many difficulties appeared on a larger scale, which troubles had not been encountered in the pilot plant. The first plant was far from an operating success. Even if the plant had operated, expected production costs were shown to be far too optimistic. After an intensive period of new process development, re-design and new engineering, a markedly different plant emerged after further large investments of capital.

The processes for the manufacture of the material were developed by the technical and engineering staff of the Electro Manganese Corporation and are based on fourteen United States and numerous foreign patents owned by the corporation.

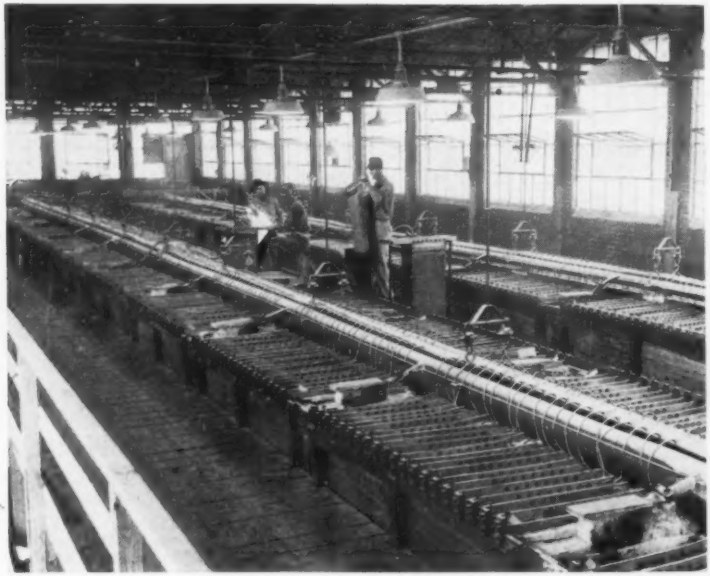
After the Electro Manganese Corporation had produced nearly 2,000,000 pounds of material, the Bureau of Mines set up and operated an experimental plant at Boulder City, Nevada. Over a five-year period, this unit made 1,500,000 pounds of manganese up to the time it was closed down. This work has been the subject of numerous papers and the operations have been described by Jacobs, Hunter, Yarroll, Churchward, and Knickerbocker (4).

Operating conditions at Boulder City were as follows:

Anode	99 per cent Pb, 1 Ag. 15 x 32 x ¼ in. 40 per cent void. 28 anodes per cell.
Cathode	Type 316 stainless steel. 18 x 36 x 16-in. gauge. 27 cathodes per cell.
Current density	Anode: 81 to 90 amp. per sq. ft.
	Cathode: 45 to 50 amp. per sq. ft.
Cell voltage	5.0 to 5.3
Feed solution	Mn: 34 to 36 grams per liter.
	$(NH_4)_2SO_4$: 135 to 140 grams per liter.
	SO_2: 0.15 gram per liter.
Catholyte	Mn: 8 to 10 grams per liter.
	$(NH_4)_2SO_4$: 155 grams per liter (calculated from ammonia content).
	SO_2: 0.10 gram per liter.
Anolyte	Mn: 8 to 10 grams per liter.
	$(NH_4)_2SO_4$: 135 to 140 grams per liter.
	H_2SO_4: 43 to 50 grams per liter.

Diaphragm	18-oz. canvas.
Duration of electrolysis	24 hr.
Pounds Mn per cathode	10 to 12.
Current efficiency	60 to 65 per cent.

Wanamaker described the earlier Electro Manganese Corporation operations at Knoxville (5). A portion of the cell room is shown in Fig. 2.



Courtesy Electro Manganese Corporation

FIG. 2. Portion of cell room for electrolytic manganese

Manganese metal of high purity may be made by electrowinning in contrast to the special ore requirements for electric furnace processes producing less pure manganese metal. A wide variety of ores, ranging from Chamberlain, S. D., and Arkansas carbonates, imported high-grade oxides mixed with local oxide tailings plus by-product solution from a near-by chemical plant, have been used. Oxide ores are not soluble in anolyte but must be reduced. The use of carbonate ores proved, in spite of their direct solubility, to be more expensive than reduced oxide ores, because of higher freight costs per unit of manganese coupled with very high acid consump-

tion and large amounts of residue. Most ores can be successfully treated but obviously the lower grade ore mixtures require more equipment for such steps as grinding, reduction, settling, and filtering. Average grade of ore mixture is 32 per cent manganese.

The flowsheet of the process is given in Fig. 3 and the operating data for the plant in Table II.

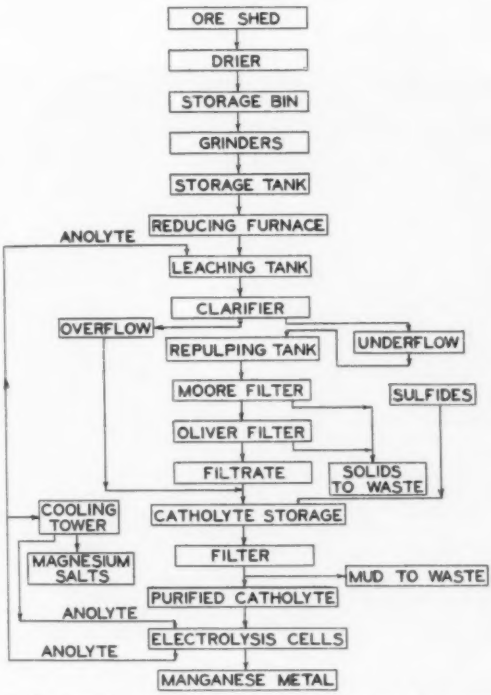


FIG. 3. Process flowsheet for the electrowinning of manganese

In the preparation of electrolyte from which the metal is deposited, the solution is purified completely of impurities such as iron, arsenic, antimony, tin, lead, nickel, cobalt, molybdenum, silica, aluminum, while calcium and magnesium are removed by special methods. At Knoxville, diaphragms are around the cathodes and the anolyte fills the cell around the diaphragms.

Numerous problems were encountered in putting the process on a commercially successful basis; among them: (1) control of magnesium in the electrolyte, (2) cell cooling, and (3) evaporation of electrolyte to make room for the leach-residue wash waters.

It should be noted that nearly all manganese ores carry magnesium, this being notably true of some of the largest domestic deposits, such as Three Kids, Chamberlain, and Emma mine. As a result, solutions in an electrolytic manganese plant are normally saturated with magnesium and calcium. Unless this magnesium is satisfactorily removed, it will even-

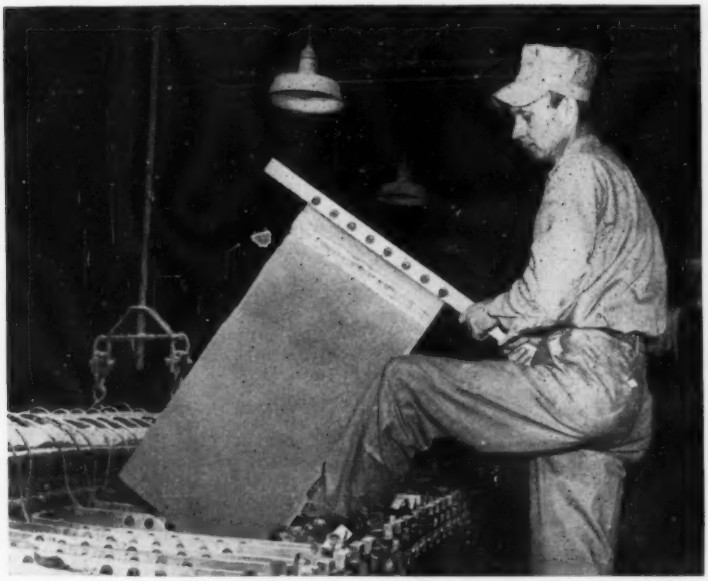
TABLE 2. *Data on production of electrolytic manganese*

Operating details	Electro Manganese Corporation, Knoxville, Tennessee
Average manganese content of ore, per cent	48
Coarse grinding	Jaw crusher and gyratory
Fine grinding	Raymond mill
Reduction furnace	2—12 in. I.D. alloy steel tubes 15 ft. long with 15 ft. cooler
Heating method	Resistance by Nichrome units
Furnace capacity, ore per day per furnace	15 tons
Reduction, per cent	99
Thickeners, Dorr	2—40 ft. diam., 90,000 gals. each
Leaching tanks	6—8,000 gals. each
Purification tanks	8—10,000 gals. each
Anolyte	
Mn, grams per liter, as $MnSO_4$	10– 18
H_2SO_4, grams per liter	25– 35
$(NH_4)_2SO_4$, grams per liter	120–140
pH value	1– 1.4
Catholyte feed	
Mn, grams per liter, as $MnSO_4$	25 – 35
$(NH_4)_2SO_4$, grams per liter	125 –135
pH value	7.2– 7.6
Anodes	
Material	Lead alloy
Number per cell	21
Cathodes	
Material	Stainless steel
Size, in.	36 x 18 x $\frac{1}{16}$
Number per cell	20
Cell amperage	6,000
Cell temperature, °C.	35–40
Cathode C.D., amp. per cell	40
Diaphragm material	Woven textile
Cell voltage	5
Current efficiency, per cent	65–70
Recovery to metal, per cent	87
Operating time for cathodes, hr.	24–40
Kw.-hr. per lb. metal (D.C.)	4– 4.5
Kw.-hr. per lb. metal (A.C. overall)	5– 5.25
Purity of manganese, per cent	99.97

tually crystallize. This usually takes place in the most inaccessible spots, such as pipe lines or pumps. Any appreciable drop in temperature of the plant electrolyte can have disastrous results by causing excessive crystallization.

At Knoxville, the three problems were solved by means including the direct evaporation of solution. A large quantity of cell anolyte is circulated over cooling towers. This circulation provides adequate evaporation to

make room for residue wash waters, sufficient cooling for holding the cell temperatures down to about 35° to 40°C. and, most important, crystallizes out at a place where it can be readily removed a complex sulfate of Mg, Ca, NH_3, and Mn which can be collected periodically and sold as a fertilizer for citrus fruit. The magnitude of the magnesium problem may be judged by the fact that the plant produced 100 tons of the complex salt during a month. This was partly due to the use of a plant feed relatively high in magnesium.



Courtesy Electro Manganese Corporation

FIG. 4. Typical cathode with manganese deposit

After many experiments, Electro Manganese Corporation developed their own anode, based on the work of Fink and Kolodney, which has a lead base and contains tin, antimony, and cobalt. This has given excellent results and has a life of over 18 months. Formation of MnO_2 is low, about 2.5 per cent of the Mn to the plant, but this is not lost, as much of it is recovered by reuse in the process. One of the problems solved at Knoxville was the development of a satisfactory cathode and process of using it. The composition of the cathode is about 18 per cent chromium, about 12 per cent nickel, and about 2 per cent molybdenum. A typical cathode in use is shown in Fig. 4.

The successful electrowinning of manganese depends upon very pure solutions.

In addition, there is dependence on a combination of factors such as concentration, pH, temperature, current density, cathode and anode material, rate of flow to the cells, as well as other variables. Problems of dealing with an alkaline catholyte and an acid anolyte in a two-compartment cell, as well as the impossibility of considering any of the variables separately because of their influence on each other, cause manganese electrowinning to be almost in a class by itself. It demands much more delicate control than does the electrowinning of zinc and copper for it carries all their problems and many more.

The product of the operation is a pure metal, is not contaminated by the constituents meticulously removed during electrolyte purification, is extremely low in carbon, and is of the order of 99.9+ per cent manganese. Average shipments are of the order of 99.97 per cent or better. The metal shows the following analysis:

Manganese	99.9+%
Nonmetals:	
Carbon	0.004%
Sulfur	0.0135%
Sulfur trioxide	not found in 25 g. sample
Sulfates	not found in 25 g. sample
Phosphorus	not found in 25 g. sample
Metals present:	
Calcium	less than 0.001%
Copper	less than 0.001%
Iron	0.001%
Magnesium	less than 0.001%
Silver	less than 0.001%

Metals absent by spectrographic analysis:

Aluminum	Cobalt	Silicon
Antimony	Lead	Tin
Arsenic	Molybdenum	Titanium
Cadmium	Nickel	Tungsten
Chromium	Potassium	Vanadium
		Zinc

It is to be noted that silicon and silica are completely absent as is also true of phosphorus. Sulfur is extremely low.

Normally, electromanganese contains 150 parts of hydrogen per million which is no particular problem for ordinary uses in the melting processes, but where necessary, metal is available with hydrogen reduced to about 5 ppm at slightly higher cost.

Electromanganese is supplied as cathode chip which is about $\frac{1}{16}$ inch thick, varying in area, and has a maximum bulk density of 178 pounds per cubic foot as packed in drums. It is shipped in 10 gallon steel drums, 250

pounds to the drum. It is also available in powder form and master alloys such as 30 Mn-70 Cu and 8 Mn-92 Al.

TABLE III. *Properties of manganese metal*

Atomic number	25
Atomic weight (1938)	54.93
Density, g./cm.³ at 20°C. (68°F.)	7.44
Density, lb./in.³ at 68°F. (20°C.)	0.268
Atomic volume, cm.³/g. atom	7.4
Melting point	1245±3°C. (2273±5°F.)
Boiling point, (760 mm. pressure)	2150°C., 3904°F.
Specific heat, cal./g./°C. at room temperature equals B.t.u./lb./°F. at room temperature	0.107
Latent heat of fusion, cal/g.	64.8
Latent heat of fusion, B.t.u./lb.	116.64
Linear coefficient of thermal expansion/°C. at room temperature	23
Linear coefficient of thermal expansion/°F. at room temperature	12.8
Type of crystal lattice	Cubic (complex)*
Lattice constant (Å = 10^{-8} cm.) 20°C. (68°F.) a_0	8.894 Å

* Ordinary form at 20°C.; other modifications known or probable at other temperatures.

TABLE IV. *Summary of data on allotropism of manganese*

Density	Form	Stability range	Crystal structure
		°C.	
7.4	Alpha	Below 730°	Body centered cubic, 58 atoms to unit cell, a = 8.894 Å
7.29	Beta	730–1100°	Body centered cubic, 20 atoms to unit cell, a = 6.300 Å
7.2	Gamma	1100–1138°	Face centered tetragonal, 4 atoms to unit cell, a = 3.767 Å c/a = 0.934
	Delta	1138–1245°	?
	Liquid	Above 1245 ±3°	

Transition points

From	To	Temperature	Condition
		°C.	
Alpha	Beta	727±3	Heating
Beta	Alpha	692–665	Cooling
Beta	Gamma	1100±3	Heating and cooling
Gamma	Delta	1138±3	Heating and cooling
Delta	Liquid	1245±3	Heating and cooling

PROPERTIES OF MANGANESE METAL

The work of a large number of investigators of the physical properties of manganese are summed up in Table III.

The vapor pressure of manganese at the triple point is given by Baukloh and Altlaid (6) as follows:

Vapor pressure mm. Hg		*Triple point °C.*
1.8		1280
0.8		1244
0.001	sublimes at	740

It has been noted that the rate of vaporization of manganese increases under the influence of a strong electric arc in vacuum—at 800°C. it doubled, at 900°C. it increased 72 per cent, at 1000°C., 8 per cent and above that

TABLE V. *Properties of manganese*

Electrical resistance		
Alpha	700×10^{-6}	Brunke[1]
	170×10^{-6}	Grube,[2] Johannsen and Nitka[3]
	210×10^{-6}	Valentiner and Becker[4]
	164×10^{-6}	Broniewski and Jaslan[5]
	150 to 616×10^{-6}	Meissner and Voigt[6]
Beta	90×10^{-6}	Brunke[1]
	100×10^{-6}	Reddemann[7]
Temperature coefficient of electrical resistance		
Alpha (0 to 700°C.)	3×10^{-6}	Johannsen and Nitka[3]
Gamma (room temperature)	39×10^{-4}	Valentiner and Becker[4]
Temperature coefficient of expansion		
Alpha	1.7×10^{-4}	Brunke[1]
(0 to 100°C.)	19.7×10^{-6}	Johannsen and Nitka[3]
(20 to 725°C.)	37.0×10^{-6}	Johannsen and Nitka[3]
Technical		
Mn (20 to 725°C.)	30.8×10^{-6}	Johannsen and Nitka[3]
(20°C.)	18.0×10^{-6}	Broniewski and Jaslan[5]
Beta	13×10^{-6}	Brunke[1]
(20 to 760°C.)	42×10^{-2}	Johannsen and Nitka[3]
Gamma	53×10^{-4}	Brunke[1]
Magnetic properties		
Alpha, chi	9.6×10^{-6}	Wheeler[8]
Beta, chi	8.8×10^{-6}	Wheeler[8]
Beta, chi	9.0×10^{-6}	Valentiner and Becker[4]

[1] F. Brunke, "Investigations on Pure Alpha, Beta, and Gamma Manganese," *Ann. Physik* **21**, 139-168 (1934).

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there was little effect. In a 24 per cent manganese iron-manganese alloy the manganese alone vaporized.

In 1925, Bradley (7) and Westgren and Phragmen (8) announced that three allotropic forms of manganese existed. These are now known as alpha, beta, and gamma. A little later Gayler (9) and Yoshisaki (10) determined the transition points for manganese made by vacuum distillation

using thermal analysis, as well as density and dilatometric methods. They obtained data showing three discontinuities. Grube (11, 12) and his coworkers observed three discontinuities in the thermal analysis data as well as that obtained by magnetic susceptibility methods applied to manganese produced by vacuum distillation. The suggestion was made that a fourth form of manganese existed. This is now referred to as delta. Sieverts and Moritz (13) studied the changes in hydrogen solubility of pure manganese. Potter and Lukens (14) from their hydrogen-solubility studies on electrolytic manganese and the data of Naylor (15) on heat content, also of the same material, suggested the temperatures in Table IV as the transition points of manganese metal.

The alpha and beta forms are brittle and hard enough to scratch glass. Gamma manganese is stated to be flexible and soft, can be bent and cut with scissors, and cannot be ground in a mortar. It is reported that electrolytic gamma manganese changes to the alpha form at ordinary temperatures.

There is a variation in the values of properties of manganese as determined by different experimenters as shown in Table V.

Any discussion of this paper will appear in the discussion section of Volume 94 of the Transactions of the Society.

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ELECTRODEPOSITION OF COBALT-TUNGSTEN ALLOYS FROM A CITRATE BATH[1]

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ABSTRACT

An aqueous bath suitable for the electrodeposition of cobalt-tungsten alloys, containing approximately 50 per cent tungsten, is described. The bath contains cobalt sulfate, sodium tungstate, and citric acid in the approximate mole ratio of 1:1:1.5. A bath pH of about 7 is most satisfactory and is obtained by the addition of ammonium hydroxide. The bath temperature should be 70°C. or above. A cathode current density of 15 amp./dm.^{2} is suitable, although lower current densities decrease the tungsten content of the deposit only slightly and result in higher current efficiencies. Bright cathode deposits are obtained over a wide range of current densities. Anodes of cobalt or of tungsten, of both of these metals, or of some inert material may be used.

INTRODUCTION

It has been known for some time that cobalt is one of the metals that codeposits with tungsten from aqueous solutions (1); since then, the electrodeposition of tungsten-cobalt (2) and tungsten-cobalt-nickel (3) alloys has been described. These previously reported baths, as well as the fluoride baths of Armstrong and Menefee (4), give alloys containing relatively small amounts of tungsten. In 1946 the citrate bath for the deposition of tungsten-nickel alloys was described (5) and in that report it was mentioned that tungsten-cobalt alloys could be plated from the same type of bath. Recently, Brenner, Burkhead, and Seegmiller (6) investigated the electrodeposition of alloys of tungsten with nickel, iron, and cobalt from baths containing salts of various hydroxy-organic acids. Since the citrate bath gives alloys containing about 50 per cent tungsten, a more complete investigation of the electrodeposition of cobalt-tungsten alloys from this type of bath seemed desirable.

The purpose of this investigation was to determine the conditions at which cathode deposits containing a maximum amount of tungsten could be obtained from the ammoniacal citrate bath, and, at the same time, to present a reasonably complete survey of the results obtained by systemati-

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cally changing, in succession, each of the variable factors while maintaining all other conditions at their optimum value for giving a cathode deposit of high tungsten content. It is believed that such a "cross-section" can be used to advantage as a line of departure by those whose interests are primarily in the development of practical plating baths, while at the same time supplying data which may prove to be of value in solving the problem of the mechanism involved in the electrolytic reduction of aqueous tungstate solutions. The effect of variations in conditions and bath composition was reflected mainly by changes in cathode current efficiency and the tungsten content of the cathode deposit.

METHODS AND MATERIALS

The plating bath

The following materials were used for preparing the baths: $Na_2WO_4 \cdot 2H_2O$, reagent grade; $CoSO_4 \cdot 7H_2O$, purified technical; and citric acid, U.S.P. Baths were in most cases prepared directly from the crystalline reagents, although stock sodium tungstate solutions were used occasionally. The baths were made up to the desired concentration and the pH was adjusted by the addition of concentrated ammonia water or, in the case of very low pH baths, by the addition of dilute sulfuric acid. The pH was determined by a glass electrode at the operating temperature of the bath except that for bath temperatures above 70°C. the pH was measured at 70°C.

Electrolysis

The electrolysis apparatus consisted of a rectifier, a variable resistance, an ammeter, a voltmeter, a copper coulometer, and from one to four electrolysis cells. Multiple electrolysis cells were used at 70°C. only and were kept at that temperature by immersion in a thermostat. Pyrex beakers served as electrolysis cells and 200 to 225 ml. of plating solution were used in each cell. Cathodes, 3 x 3 cm., were cut from electrolytic copper foil and were carefully cleaned. Cathode current efficiency calculations were based on the weight of the copper deposited in the coulometer and the gain in weight of the cathodes in the plating cells. Since the equivalent weights of tungsten and cobalt are very nearly equal, 30.7 and 29.5 respectively, a mean equivalent weight of 30.0 was used for calculations of cathode current efficiencies. The maximum error possible from such an approximation would occur in the hypothetical case of a plate of 100 per cent tungsten and would amount to only 2.3 per cent. Platinum anodes were ordinarily used, but when cobalt or tungsten anodes were used the anode current efficiencies were based on the loss in weight of these soluble anodes.

Analysis of deposits

The cathode deposits to be analyzed were first treated with nitro-hydrochloric acid or if necessary with nitric and hydrofluoric acids. Tungsten was determined gravimetrically by the Yoe-Jones method (7). Copper was removed by electrolysis from a sulfuric acid solution and then the cobalt was determined by deposition on a platinum gauze cathode from a strongly ammoniacal solution.

EXPERIMENTAL

Preliminary work indicated that high-tungsten-content cathode deposits were obtained at the following conditions: cathode current density 15 amp./dm.^{2}, bath temperature 70°C., bath pH approximately 7, and with 66 g./l. of citric acid in the bath. In the first series of experiments, these conditions were kept constant while the optimum Co/W mole ratio in the bath was being determined. Then, when the best Co/W ratio had been determined, it was maintained constant while each of the above mentioned conditions was varied in turn. Platinum anodes were used, but the time of electrolysis was short enough to minimize changes of bath pH during electrolysis. Freshly-prepared baths were used for each electrolysis run.

Cobalt in the bath

In determining the effect of variations in the cobalt content of the bath, the above mentioned conditions were maintained and, in addition, the tungsten in the bath was arbitrarily fixed at 28 g./l. The amount of cobalt was varied from 0.5 to 12.6 g./l. and the results are given in Fig. 1. As would be expected, the plates with the highest tungsten content (about 56 per cent W) were obtained from the bath with the lowest cobalt content. It can be seen also that, in general, cathode current efficiency increases as the cobalt content of the bath is increased. All the cathode deposits were bright and metallic in appearance.

Tungsten in the bath

The cobalt content of the bath used to determine the effect of variations of the amount of tungsten was fixed at 12.6 g./l. and the other conditions were again kept constant. The amount of tungsten in the bath was varied from 1.7 to 55.7 g./l. and the results are given in Fig. 2. Cathode deposits with a maximum tungsten content were obtained when the bath contained about 44.5 g./l. of tungsten. Cathode current efficiency was found to decrease slightly as the tungsten content of the bath was increased. All of the plates were bright.

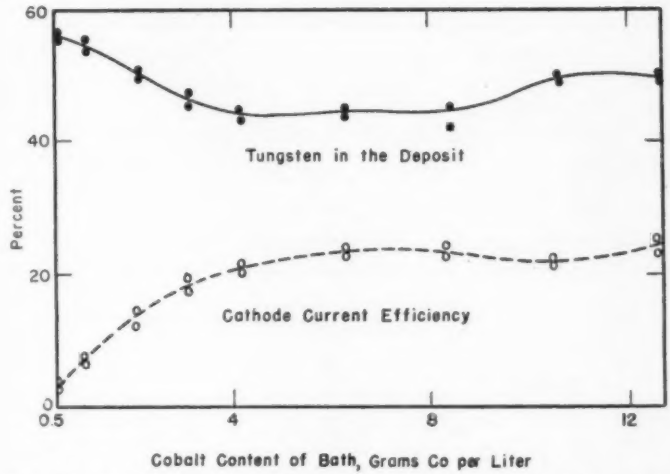

FIG. 1. The effect of changing the cobalt concentration of the bath. Tungsten, 28 g./l.; citric acid, 66 g./l.; temp. 70°C.; C.C.D. 15 amp./dm.^{2}; pH 7.

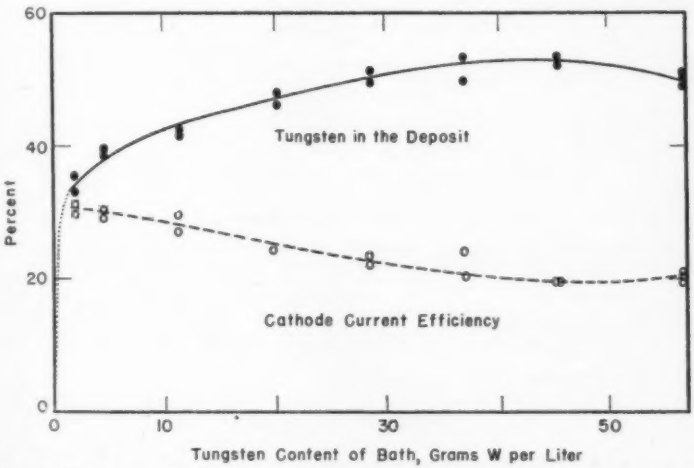

FIG. 2. The effect of changing the tungsten content of the bath. Cobalt, 12.6 g./l.; citric acid, 66 g./l.; temp. 70°C.; C.C.D. 15 amp./dm.^{2}; pH 7.

Citric acid in the bath

On the basis of the above described results, it was decided that, for additional work, the cobalt content of the bath would be fixed at 12.6 g./l.[2] and

[2] 12.6 g./l. Co = 60 g./l. $CoSO_4 \cdot 7H_2O$; 39.3 g./l. W = 70 g./l. $Na_2WO_4 \cdot 2H_2O$

the tungsten content at 39.3 g./l.,[2] which gives a 1:1 mole ratio of W/Co in the bath. The effect of variations in the citric acid content of this bath is given in Fig. 3. The results confirm the previous observation that about 66 g./l. of citric acid is the most satisfactory. It can be seen that both cathode current efficiency and tungsten content of the deposit decrease as the citric acid in the bath is increased. All the cathode deposits were bright.

Bath temperature

The effect of temperature variations on the performance of the bath is shown in Fig. 4. The tungsten content of the plates reaches a maximum at

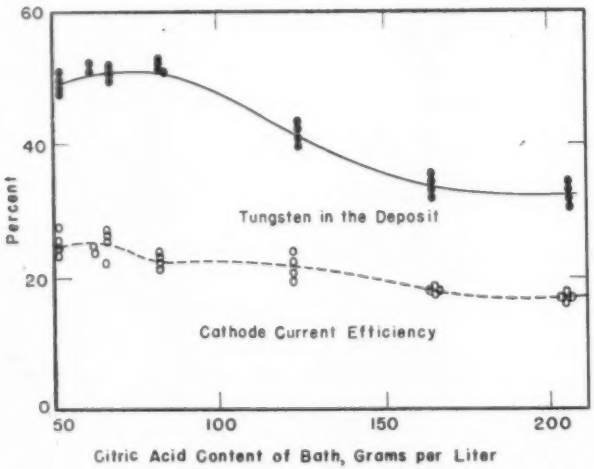

FIG. 3. The effect of changing the citric acid concentration of the bath. Cobalt, 12.6 g./l.; tungsten, 39.3 g./l.; temp. 70°C.; C.C.D. 15 amp./dm.^{2}; pH 7.

a bath temperature of 70°C. with no further increase at higher temperatures. It can also be seen that cathode current efficiency is greater at the higher bath temperatures.

Cathode current density

Fig. 5 shows the effect of cathode current density variations on the performance of the bath. These variations have very little effect on the amount of tungsten in the cathode deposit, but there is a marked decrease in cathode current efficiency as the current density is increased. It was observed that deposits obtained at the lower current densities had a greater mechanical strength than those obtained at the higher current densities, which is in agreement with the results reported by Brenner *et al.* (6).

Bath pH

Fig. 6 shows the marked effect of bath pH on the tungsten content of the deposits and on the cathode current efficiency. A bath pH of 7 gives a

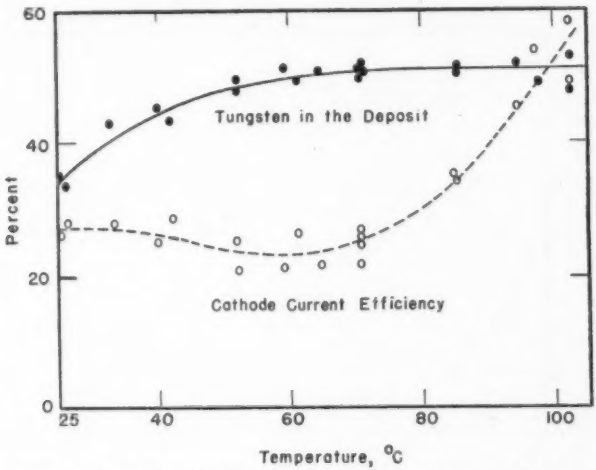

FIG. 4. The effect of changing the temperature of the bath. Cobalt, 12.6 g./l.; tungsten, 39.3 g./l.; citric acid, 66 g./l.; C.C.D. 15 amp./dm.²; pH 7.

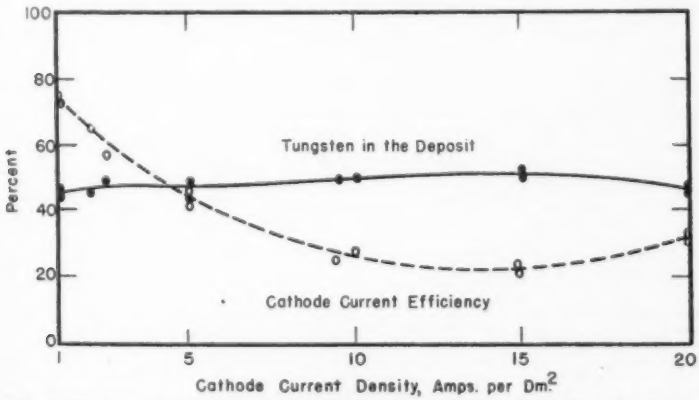

FIG. 5. The effect of changing the cathode current density. Cobalt, 12.6 g./l.; tungsten, 39.3 g./l.; citric acid, 66 g./l.; temp. 70°C.; pH 7.

maximum tungsten content in the deposit but a minimum cathode current efficiency.

Hull cell

This cell was used to find the bright plating range of the bath at a number of different pH values and the results are given in Table I. The best plates were obtained at pH 7; plates at pH 8.5 were quite satisfactory, but

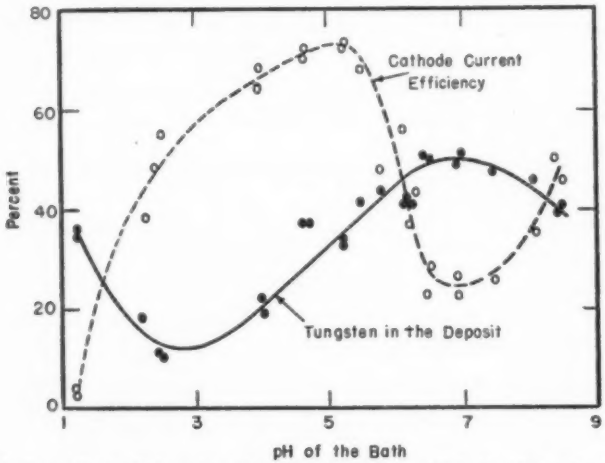

FIG. 6. The effect of changing the pH of the bath. Cobalt, 12.6 g./l.; tungsten, 39.3 g./l.; citric acid, 66 g./l.; temp. 70°C.; C.C.D. 15 amp./dm.^{2}

TABLE I. *Hull cell results showing the effect of bath pH on the bright plating range*

Cobalt, 12.6 g./l.; tungsten, 39.3 g./l.; citric acid, 66 g./l.; total current 5 amperes; temp. 70°C.; 5 min. electrolysis.

pH of the bath	Bright plating range Amp./dm.^{2} (approx.)
2.4	No bright plates
3.9	No bright plates
4.6	5 to 9 amp./dm.^{2}
5.1	5 to 11 "
5.6	4 to 12 "
6.0	2 to 8 "
7.0	2 to 20 "
8.5	3 to 12 "

at higher current densities they showed a tendency to crack and peel, which observation also agrees with the results reported by Brenner *et al.* (6). It should be mentioned that for baths of pH 5.6 and above a fairly definite milky line marked the lower limit of the bright range. At still lower current densities bright plates were again obtained.

Anodes

The platinum anodes used in this work were usually coated with a thin black deposit which appeared to be a higher oxide of cobalt together with some tungsten compound. When cobalt or tungsten anodes were used, the rate at which they went into solution varied considerably with the pH. For example, at an anode current density of 3.5 to 4 amp./dm.^{2} tungsten anodes, which went into solution with an efficiency of about 20 per cent at pH 3, went into solution with 100 per cent efficiency when the pH was about 7 or above. Cobalt anodes went into solution with somewhat greater than 100 per cent efficiency when the pH was 6 or below; however, in the pH range 6 to 7.5 the rate of solution decreased sharply, and a heavy, pink, semi-adherent corrosion product appeared which dissolved slowly on stirring. When the pH was above 8, the rate of anode solution increased rapidly.

Bath stability

In general the bath seemed to be quite stable although on standing or cooling some of the more concentrated baths gave a small amount of a pink precipitate which was soluble in an excess of citric acid. When the used baths were allowed to evaporate somewhat, a few green crystals often appeared. These evaporation products seemed to have no deleterious effects on the bath. The absolute concentration of the bath was found to be not very critical, since on dilution to almost five times the original volume, the cathode current efficiency and tungsten content of the deposit were reduced only slightly.

CONCLUSIONS

The following bath for the electrodeposition of cobalt-tungsten alloys is proposed: cobalt, as $CoSO_4 \cdot 7H_2O$, 12.6 g./l.; tungsten, as $Na_2WO_4 \cdot 2H_2O$, 39.3 g./l.; citric acid, 66 g./l.; and NH_4OH to pH 7. This bath should be operated at 70° to 90°C. and at a cathode current density of 2 to 15 amp./dm.^{2}

Cobalt, tungsten, cobalt and tungsten, or insoluble anodes may be used, but in all cases it is necessary to make proper adjustment of bath pH during longer periods of electrolysis. At a pH of 7, when soluble anodes are used, agitation may be necessary to aid in the solution of anode corrosion products.

The cathode deposits obtained from this bath at 15 amp./dm.^{2} contain about 50 per cent tungsten. The plates are quite bright and show no tendency to tarnish. Plates obtained at lower current densities seem to have greater mechanical strength, although they contain slightly less tungsten.

The absolute concentration of this bath is not very critical, but the opti-

mum mole ratio of cobalt, tungsten, and citric acid seems to be about 1:1:1.5.

Three bath pH values, 8.5, 7, and 4.5–5.5, merit consideration for the possible development of a practical plating bath. The high-pH bath proposed by Brenner (6) has the disadvantage of losing ammonia rather rapidly at elevated temperatures. The neutral bath has the disadvantage of relatively low cathode current efficiency. The deposits from the acid bath appear somewhat weaker than the others and there is more of a tendency toward pitting.

Any discussion of this paper will appear in the discussion section of Volume 94 of the Transactions of the Society.

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CODEPOSITION OF TUNGSTEN AND IRON FROM AN AQUEOUS AMMONIACAL CITRATE BATH[1]

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ABSTRACT

This new aqueous plating bath for the electrodeposition of iron-tungsten alloys is an additional contribution to the general subject—the electrolytic reduction of aqueous tungstate solutions. The experimental work was carried out with three baths having different concentrations of sodium tungstate. The performance of these baths and the effect of variations in bath composition and electrolysis conditions were measured by changes in cathode current efficiency and in the composition and appearance of the cathode deposits. The following bath is proposed for the electrodeposition of iron-tungsten alloys: tungsten, as $Na_2WO_4 \cdot 2H_2O$, 28 g./l.; iron as 50 per cent Fe^{II} and 50 per cent Fe^{III}, 2 g./l.; citric acid 66 g./l.; and NH_4OH to pH 8. This bath should be operated at about 70°C. and at a cathode current density of approximately 5 amp./dm.^{2} The cathode deposits obtained contain about 50 per cent tungsten. This ammoniacal citrate bath is also suitable for the electrodeposition of nickel-tungsten and cobalt-tungsten alloys.

[1] Manuscript received July 15, 1948. This paper prepared for delivery before the New York Meeting, October 13 to 16, 1948.

INTRODUCTION

In a previous paper in this series, describing the codeposition of tungsten and nickel from an aqueous ammoniacal citrate bath (1), it was mentioned that tungsten and iron could be codeposited from the same type of bath. The observation that tungsten-iron alloys can be electrodeposited from aqueous solutions is not new; the carbonate bath (2) and the sulfate bath (3) were reported several years ago. Recently, Brenner and coworkers (4) reported the electrodeposition of tungsten alloys containing iron, nickel, and cobalt from ammoniacal plating solutions containing salts of various hydroxy-organic acids. Continued interest in the electrodeposition of tungsten alloys seemed to justify a further investigation of the ammoniacal citrate bath for the codeposition of tungsten and iron, and this paper is a description of that work. It should be mentioned that the development of a practical plating bath was not of major interest; rather the primary aim was to contribute additional information to the broader general subject—the electrolytic reduction of aqueous tungstate solutions.

In the experimental work three baths having different concentrations of sodium tungstate were used: (a) a low tungsten bath, (b) a high tungsten bath, and (c) a medium tungsten bath. The performance of these baths and the effect of variations in bath composition and electrolysis conditions were measured by changes in cathode current efficiency and the composition and appearance of the cathode deposits. Cathode current efficiencies were based on the analysis of the plate and the oxidation state of the iron used in preparing the bath. It is recognized that these current efficiency calculations are not exact, but the values obtained serve to compare the efficiencies of the various baths used.

EXPERIMENTAL TECHNIQUES

Electrolysis

The electrolysis set-up was essentially the same as that previously described (1). Direct current was supplied by a variable voltage selenium rectifier. Bath temperatures were maintained by means of a thermostat. Copper foil cathodes, 3 x 3 cm., and sheet iron anodes were used. A copper coulometer in series with the plating cells made it possible to calculate current efficiencies. Electrolysis runs, usually of 20 minutes duration, were carried out in duplicate and checked further if necessary.

Bath preparation

Tungsten was added to the baths as sodium tungstate, $Na_2WO_4 \cdot 2H_2O$. The iron compound used in each bath is indicated in the appropriate places. It was found best to add the citric acid to the tungstate solution before adding the iron salt. The pH was determined by a glass electrode at the

operating temperature of the bath. The amount of citric acid in the bath, 66 g./l., was selected rather arbitrarily on the basis of experience with other similar baths.

Analysis of deposits

The alloy deposits to be analyzed were treated with nitro-hydrochloric acid or if necessary with hydrofluoric and nitric acids. Tungsten was determined gravimetrically by the cinchonine method. Iron was determined volumetrically by a method involving precipitation of the hydroxide, ashing, fusion with potassium hydrogen sulfate, leaching with hydrochloric acid, reduction with tin (II) chloride, and titration with dichromate solution using diphenylamine indicator. When the details of this volumetric method were worked out it was found to be rapid and quite accurate. Since some of the samples were rather small, an analysis giving a total of iron and tungsten of 96 to 99 per cent was considered satisfactory.

THE LOW TUNGSTEN BATH

This bath had the following composition: tungsten 2 g./l.; iron, as $FeSO_4 \cdot 7H_2O$, 17.5 g./l.; citric acid 66 g./l.; triethanolamine, 27 g./l.; and ammonium hydroxide to pH 8. When used at 70°C. and 5 amp./dm.^{2} it gave a deposit containing 52 per cent tungsten at a cathode current efficiency of 40 per cent.

Triethanolamine

This amine acted as a brightener, but it decreased the cathode current efficiency somewhat. In its absence the cathode deposits were dull and tarnished; when it was added to the bath in increasing amounts the plates became brighter with about 27 g./l. being the most satisfactory. It had no apparent effect on the amount of tungsten in the plate.

Bath pH

A bath pH of 8 was found to be the best when the usual electrolysis conditions were used. Cathode current efficiency (40 per cent) and the amount of tungsten in the deposit (52 per cent) were about the same at pH 7 and 8; however, at pH 9 both decreased sharply—current efficiency to 32 per cent and tungsten content to about 26 per cent. The best appearing plates were obtained at pH 8.

Cathode current density

Changes in cathode current density had a marked effect on both current efficiency and the amount of tungsten in the deposit. As can be seen from the results given in Table I the tungsten content reached a maximum at 5 amp./dm.^{2} whereas the current efficiency reached a maximum at 2 amp./dm.^{2} and then dropped off sharply.

Bath temperature

When this low tungsten bath was used at room temperature, the cathode deposits were inferior in appearance and both tungsten content of the deposit and cathode current efficiency were lower than at 70°C. A bath temperature higher than 70°C. was not used since it was felt that bath pH maintenance would then become a problem.

THE HIGH TUNGSTEN BATH

This bath had the following composition: tungsten 56 g./l.; iron as $FeSO_4 \cdot 7H_2O$, 2 g./l.; citric acid 66 g./l.; triethanolamine 27 g./l.; ammonia to pH 8. When used at 70°C. and 5 amp./dm.^{2} it gave a deposit containing 56 per cent tungsten at a current efficiency of about 27 per cent.

TABLE I. *The effect of cathode current density changes on the low tungsten bath* 2 g./l. W; 17.5 g./l. Fe; pH 8; temp. 70°C.

Cathode current density, amp./dm.^{2}	1	2	3	4	5	10
Per cent tungsten in the deposit	40.9	44.0	49.4	48.5	52.5	38.6
Cathode current efficiency (per cent)	50.5	68.5	56.3	49.0	41	39.7
Appearance of the cathode deposit	Dull	Dull	Dull	Bright	Bright	Bright

TABLE II. *The effect of current density changes on the high tungsten bath* 56 g./l. W; 2 g./l. Fe; pH 8; temp. 70°C.

Cathode current density, amp./dm.^{2}	1.0	1.5	2.0	3.0	4.0	5.0	10.	15
Per cent tungsten in the deposit	58.1	—	57.2	57.2	57.8	56	57.8	62.2
Cathode current efficiency (per cent)	26.2	32	46.0	42.1	36.3	27	23.6	21.0

Triethanolamine

Triethanolamine acted as a brightener in this bath just as it did in the low tungsten bath. Variations in the amount seemed to have no marked effect on cathode current efficiency or on the amount of tungsten in the cathode deposit.

Bath pH

A pH of 8 was found most satisfactory for this bath also, although the cathode deposits contained somewhat more tungsten when they were obtained from a pH 7 bath. Plates from the pH 9 bath were somewhat tarnished. Cathode current efficiency was not affected by changes in bath pH over the range studied—pH 7, 8, 9.

Cathode current density

As can be seen from the results given in Table II, current density changes had only a small effect on the tungsten content of the deposit but a marked effect on cathode current efficiency. The deposits were all bright.

Iron in the bath

The results given in Table III show that the amount of iron in this bath has an effect on both cathode current efficiency and the amount of tungsten in the deposit. All the deposits were bright.

Tungsten in the bath

Decreasing the amount of tungsten in this bath to about 14 g./l. had little effect on cathode current efficiency and decreased the amount of tungsten in the cathode deposit only a small amount. This suggested that a bath of medium tungsten concentration should be satisfactory.

TABLE III. *The effect of changes of iron concentration on the high tungsten bath*
56 g./l. W; pH 8; temp. 70°C.; C.C.D. 5 amp./dm.²

Iron in the bath, g./l.	0.2	0.8	2.0
Per cent tungsten in the deposit	65.5	58.0	56
Cathode current efficiency (per cent)	3.6	10.0	27

TABLE IV. *A comparison of Fe^{II} and Fe^{III} medium tungsten baths*
2 g./l. Fe; 28 g./l. W; 66 g./l. citric acid; pH 8; temp. 70°C.; 5 amp./dm.²

	Fe^{II} Baths		Fe^{III} Baths	
	Fresh	36 days	Fresh	27 days
Per cent tungsten in the deposit	61.4	56.9	52.2	55.5
Cathode current efficiency (per cent)	9.7	19.3	33.8	22.0

THE MEDIUM TUNGSTEN BATH

This bath had the following composition: tungsten 28 g./l.; iron 2 g./l.; citric acid 66 g./l.; ammonia to pH 8; no triethanolamine. Usual electrolysis conditions were 70°C. and 5 amp./dm.²; but conditions and bath composition were varied as indicated.

Fe^{II} and Fe^{III} in the bath

It is obvious that iron (II) compounds used in preparing these iron-tungsten baths are readily oxidized. This oxidation affected the performance of the baths and, in order to obtain reproducible results, it was found necessary to use the iron (II) baths as soon as they had been prepared. Fe^{III} baths were found to give greater cathode current efficiency but the deposit contained less tungsten than the comparable Fe^{II} baths. The results of a comparison of Fe^{II} and Fe^{III} baths containing the same total amount of iron when used immediately (fresh) and after standing several weeks are given in Table IV. It can be seen that both baths change on standing and give cathode current efficiency and tungsten content values which are more nearly alike than do the freshly prepared baths.

A study of the effect of the ratio of Fe^{II} to Fe^{III} used in preparation of the baths on the bath characteristics was made next. Iron (II) was added as ferrous ammonium sulfate and iron (III) as ferric ammonium sulfate. Various ratios from 100 per cent Fe^{II} to 100 per cent Fe^{III} were used with the total amount of iron in the bath being in all cases 2 g./l. The baths were used immediately after preparation. The results presented graphically in Fig. 1 show that as the relative amount of Fe^{III} in the bath is increased the percentage of tungsten in the deposit decreases and the cathode current efficiency increases. On the basis of these results it was concluded

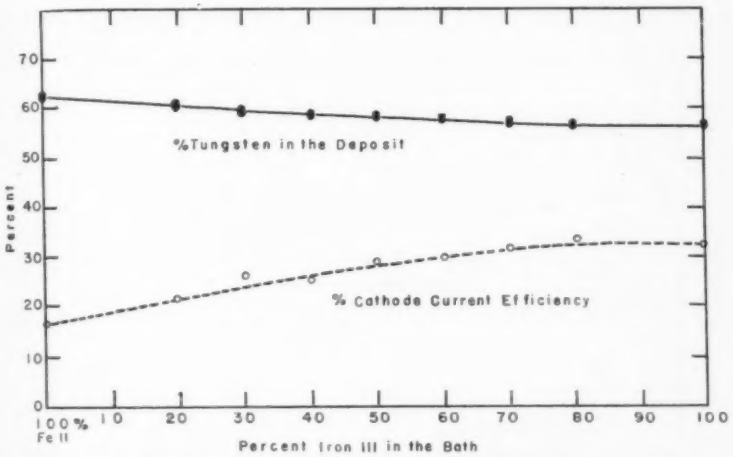

FIG. 1. The effect of the ratio of Fe^{II} to Fe^{III} on the medium tungsten bath. Total iron 2 g./l.; tungsten 28 g./l.; citric acid 66 g./l.; pH 8; temp. 70°C.; C.C.D. 5 amp./dm.^{2}

that a 1 to 1 mole ratio of Fe^{II} and Fe^{III} in the bath would give satisfactory current efficiency without unduly lowering the tungsten content of the cathode deposit.

Anodes

The iron anodes used in all the work so far described showed very little if any loss of weight on electrolysis. In some cases the anodes gained in weight slightly and were somewhat tarnished. When the anodes were half tungsten and half iron, with the same total anode area as previously used, the iron anode showed only a slight loss of weight whereas the tungsten anode went into solution with an efficiency of 90 per cent to 100 per cent. Addition of NH_4Cl to the bath in amounts up to 100 g./l. had little if any effect on the anode corrosion When the tungsten anode area was de-

creased and the iron anode area increased the amount of anode corrosion varied considerably and the results were not reproducible.

Iron in the bath

The amount of iron was varied from 2 g./l. to 21 g./l. and in all cases it was added as 50 per cent Fe^{II} and 50 per cent Fe^{III}. The effect of this variation on the tungsten content of the cathode deposit and on the cathode current efficiency is shown in Fig. 2. No corrosion of the iron anodes was observed; in fact when the mole ratio of Fe/W was $\frac{1}{4}$ (7 g./l. Fe) or higher the anodes gained weight slightly due to the formation of what appeared to be a tungsten bronze on the anode surface. Baths containing more than

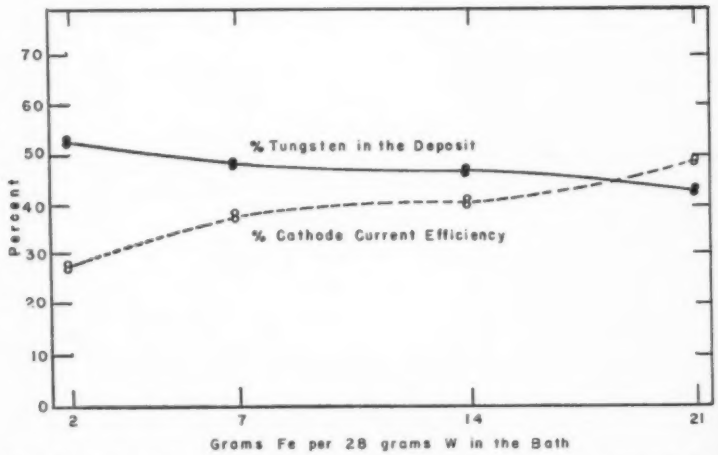

FIG. 2. The effect of changing the iron content of the medium tungsten bath. Iron as 50% Fe^{II} and 50% Fe^{III}; tungsten 28 g./l.; citric acid 66 g./l.; pH 8; temp. 70°C; C.C.D. 5 amp./dm.^{2}

21 g./l. of iron were unstable. The cathode deposits obtained from the bath with 2 g./l. of iron were bright and silvery, but showed a tendency to become slightly blue on standing. As the amount of iron in the bath was increased the plates became dull and showed a greater tendency to become stained. Triethanolamine was tried as a brightener in the bath containing 7 g./l. iron but the plates obtained were very badly stained. On the basis of this work, it was concluded that the bath containing 2 g./l. of iron gives the best appearing plates.

Bath pH

The effect of variation of bath pH on the operation of the medium tungsten bath is shown in Fig. 3. The amount of tungsten in the plate is at a

maximum at pH 7, while the cathode current efficiency is greatest at pH 6. The anode efficiency, which was over 100 per cent in the acid baths, dropped to less than 2 per cent at pH 7 and was less than 0.2 per cent at pH 8. The cathode deposits obtained from acid baths were inferior in appearance and not very resistant to nitro-hydrochloric acid. The pH 2 bath gave plates that were tarnished dark brown and blue, and the pH 6 and 7 baths gave plates that were bright at first but soon tarnished blue and brown in spots. Deposits obtained from the pH 8 bath were bright and silvery in appearance. The plates obtained from the acid baths were readily attacked

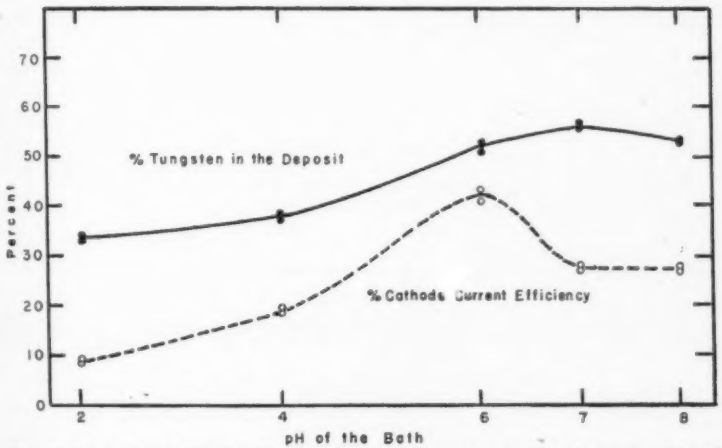

FIG. 3. The effect of bath pH on the medium tungsten bath. Tungsten 28 g./l.; iron 2 g./l. (50% Fe^{II}, 50% Fe^{III}); citric acid 66 g./l.; temp. 70°C.; C.C.D. 5 amp./dm.^{2}

by nitro-hydrochloric acid, whereas it was necessary to use hydrofluoric and nitric acids on the plates from the pH 7 and 8 baths.

Bath temperature

The effect of temperature changes on the medium tungsten bath is shown in Fig. 4. As the operating temperature of the bath was increased from 35°C. to 85°C. the tungsten content of the cathode deposit increased from 43 per cent to 58 per cent, and the cathode current efficiency increased from 20 per cent to 28 per cent. It was found also that anode current efficiency increased to 40 per cent at 85°C. whereas at the lower bath temperatures the anode efficiency was less than 2 per cent. The deposits obtained at 35°C. readily tarnished blue and brown; those from the 55°C. bath had some brown stain and acquired a bluish tinge on standing; and those from

the 85°C. bath were stained brown around the edges and showed a tendency to blister in spots. Since the plates obtained from the 70°C. bath were bright and silvery this seems to be the best temperature for operating the bath.

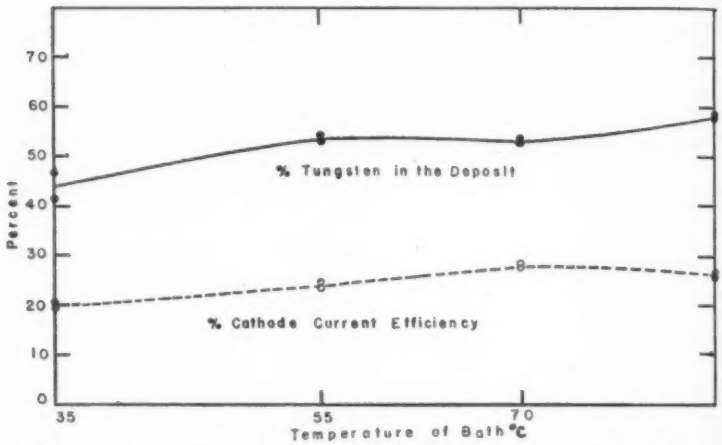

FIG. 4. The effect of bath temperature on the medium tungsten bath. Tungsten 28 g./l.; iron 2 g./l. (50% Fe^{II}, 50% Fe^{III}); citric acid 66 g./l.; pH 8; C.C.D. 5 amp./dm.^{2}

CONCLUSIONS

On the basis of the foregoing work, the following bath is proposed for the electrodeposition of iron-tungsten alloys: tungsten as $Na_2WO_4 \cdot 2H_2O$, 28 g./l.; iron, as 50 per cent Fe^{II}[2] and 50 per cent Fe^{III}[2], 2 g./l.; citric acid 66 g./l.; and NH_4OH to pH 8. This bath should be operated at about 70°C. at a cathode current density of approximately 5 amp./dm.^{2} Iron anodes should be used, although it seems likely that an iron and tungsten anode combination could be used.

The cathode deposits obtained from this proposed bath contain about 53 per cent tungsten. The plates are bright and shiny in appearance and show only a slight tendency to tarnish. They are quite resistant to attack by acids and must be treated with HF + HNO_3 for analysis.

A 1:1 mole ratio of Fe^{II} and Fe^{III} in the bath with a total of 2 g./l. of iron is recommended as it gives good cathode current efficiency and a fairly high tungsten content in the deposit. A bath containing all of the iron as Fe^{III} gives higher cathode current efficiency but the resulting deposit contains less tungsten. If only Fe^{II} is used in the bath, the cathode current effi-

[2] Fe^{II} as $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$; Fe^{III} as $FeNH_4(SO_4)_2 \cdot 12H_2O$.

ciency is less but the tungsten content of the plates is greater; also these deposits show less tendency to tarnish.

The amount of tungsten in the bath (28 g./l.) is not very critical. It can be decreased or increased somewhat without changing the characteristics of the bath appreciably.

The amount of citric acid in the bath (66 g./l.) is about the best for the iron concentration used. The baths are quite stable and show no tendency to form a precipitate on standing for several months. If the amount of iron is increased very much it is necessary to increase the citric acid concentration in order to avoid the formation of a precipitate in the bath.

This ammoniacal citrate bath is suitable for the electrodeposition of iron-tungsten, nickel-tungsten, and cobalt-tungsten alloys.

Any discussion of this paper will appear in the discussion section of Volume 94 of the Transactions of the Society.

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THE EFFECT OF PRESSURE ON CURRENT EFFICIENCY OF COPPER ELECTRODEPOSITION FROM CYANIDE SOLUTIONS[1]

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ABSTRACT

The efficiency of copper deposition from copper cyanide solutions is improved by decreasing the total pressure on the bath; also an increase in total pressure results in decreasing efficiency. A simple mathematical relationship has been developed to relate the deposition efficiency of copper with the total pressure and current density. This study has been made on only one bath at a constant temperature of 50°C. Possible applications of these results are discussed.

INTRODUCTION

No literature has been found on the electrodeposition of metals under pressures other than atmospheric, although high pressure techniques have long been in use for electrolytic hydrogen production, and low pressure technique has recently been reported in ozone production (1). A number of

[1] Manuscript received June 14, 1948. This paper prepared for delivery before the New York Meeting, October 13 to 16, 1948.

workers have investigated the effect of pressure on hydrogen over-voltage (2, 3, 4, 5, 6) but their findings do not seem to be conclusive.

Upon the suggestion of J. B. Kushner (7) this work was undertaken to discover whether the suppression of hydrogen evolution due to increased pressure, as implied by LeChatelier's principle, would in any way improve electroplating.

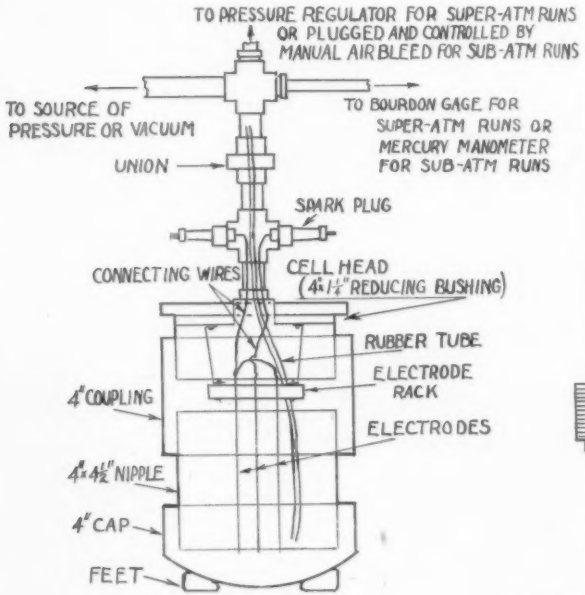

FIG. 1. The cell

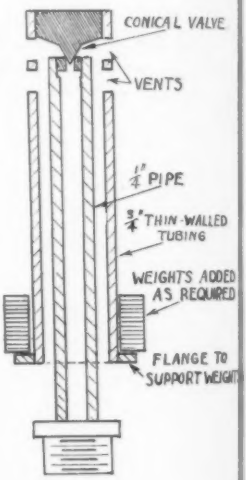

FIG. 2. Pressure regulator (dead w
relief valve)

EXPERIMENTAL PROCEDURE

The apparatus was made of standard plumbing parts as illustrated in Fig. 1, 2, and 3. The pressure regulator was used for all experiments done at pressures greater than one atmosphere. By placing ring-shaped weights on the indicated flange, the desired pressures could be obtained. For the reduced pressure runs, a "Cenco Hyvac" pump was attached to the cell and the pressure manually controlled to the desired value as indicated by an open end mercury manometer.

The number of coulombs passed was determined by the use of a copper coulometer. These data coupled with elapsed time measurements were used to calculate both current densities and current efficiencies.

The composition of the plating bath was:

CuCN	3.0 oz./gal.	(22.5 g./l.)
NaCN	4.5 oz./gal.	(33.7 g./l.)
Na_2CO_3	2.0 oz./gal.	(15.0 g./l.)

Total copper, by analysis: 0.0159 g./ml.

All experiments were conducted at 50°C.

Five gallons of electrolyte were prepared but, because of the large capacity of the cell (1230 ml.) and the desirability of using fresh electrolyte for each run, it was found necessary to regenerate the electrolyte periodically. The electrolyte was regenerated in a large cell using an iron anode and

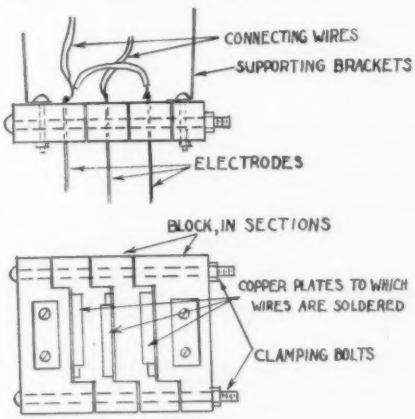

FIG. 3. Electrode rack

copper cathode, such treatment continuing until the copper content was reduced to the original value.

In normal operations the cell was disconnected at the ½-inch union and the cell head (4 in. x 1¼ in. reducing bushing) removed. The electrodes were then placed in the electrode rack and the cell head replaced and the connection made up in a pipe vise. The cell was then allowed enough time in the constant temperature bath to bring it up to temperature. Electrolyte (already at 50°C.) was then added through the rubber tube. The ½-inch union was then made up and electrolysis started as soon as possible after the desired condition of the pressure had been obtained. At the conclusion of the run, the union was broken and the electrolyte withdrawn through the rubber tube, by suction, in as short a time as possible. The cell head was removed and the electrodes were rinsed with distilled water, dried, and then weighed.

DATA AND RESULTS

The data are reported in Table I and in the figures.

TABLE I. *Gas bubbling tests*

Gas bubbled	Time	C.d.		c
	min.	*amp./ft.*	*amp./dm.²*	%
None	10	10.7	1.15	48.8
Nitrogen	10	10.3	1.11	50.9
Nitrogen	20	10.7	1.15	50.8
Nitrogen	40	10.8	1.16	52.6
Nitrogen	40	10.8	1.16	62.7
Nitrogen	40	10.5	1.13	57.9
Air	40	10.4	1.12	57.8

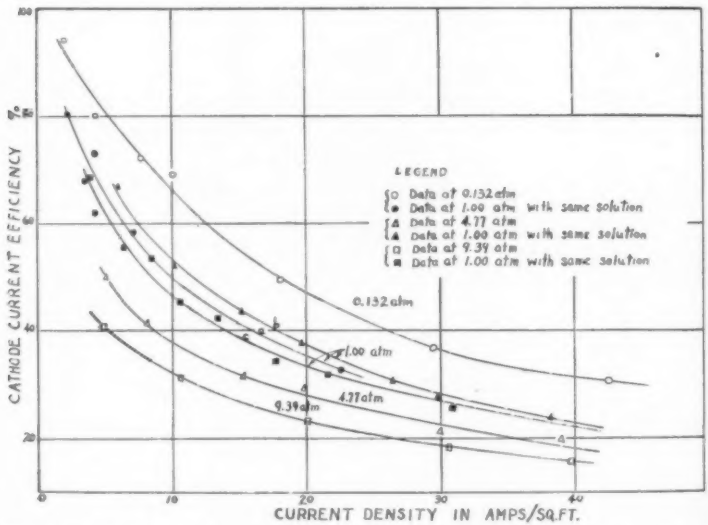

FIG. 4. The effect of pressure upon the current efficiency vs. current density relation of a copper cyanide plating bath.

DISCUSSION

The graphical presentation of the data on a linear scale in Fig. 4 shows that there is a clear and regular displacement of the efficiency-versus-current density curves due to total pressure changes. When these same data were plotted on a semi-logarithmic scale, the points fell on straight lines (Fig. 5). This permitted their expression as simple mathematical functions. The three lines at atmospheric pressure (a, b, and c) are the result

of changes in solution composition after regeneration, other than in the copper content, which had been restored to its original value. Five gallons of solution were sufficient to establish a line at atmospheric pressure and at one other condition. The solution as first made up was used at atmospheric pressure and at 4.77 atmospheres, this solution was then regenerated as described above, and, after which, it was used to establish the second atmospheric line and the line at 0.132 atmospheres. After a second regeneration, the third atmospheric line and the line at 9.39 atmospheres was determined. In the plots the atmospheric line, determined using the same solution as that used for establishing each of the other lines, can be identified, since the same symbols are used in plotting pairs of lines determined with the same electrolyte.

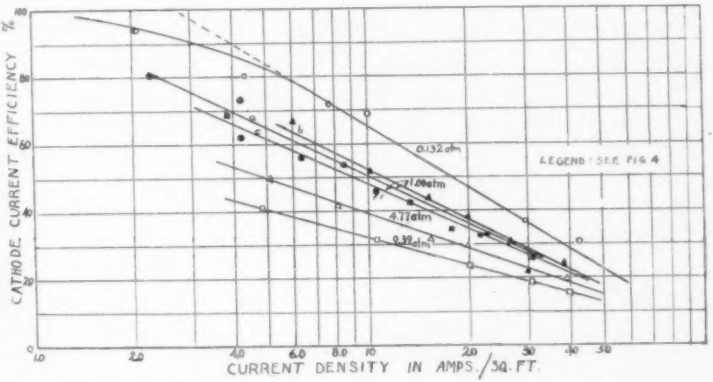

FIG. 5. The effect of pressure upon the current efficiency vs. current density relation of a copper cyanide plating bath (direct semi-log plot).

In order that the data might be converted to a common atmospheric line, a trial cross plot on semi-logarithmic paper was made. In this trial plot, lines of constant current density were drawn relating current efficiency to pressure. These were very nearly straight lines, which could be expressed by the following equation:

$$\epsilon_c = \epsilon_c'' + m \ln p$$

Therefore, the rate of change of the current efficiency with change in pressure may be obtained by differentiating the above equation thus:

$$\frac{d\epsilon_c}{dp} = \frac{m}{p}$$

This shows that the rate of change of current efficiency with respect to pressure is proportional to the reciprocal of the pressure. The line, cor-

responding to the 0.132 atmosphere line, was chosen as standard. Therefore, the 4.77 atmosphere line would have to be lowered to the extent of $\frac{1}{4.77}$ times the distance that the corresponding atmospheric line is lowered. The excellence of the correlation thus obtained supports this procedure.

The corrected lines are plotted in Fig. 6. Here the tendency to converge is clearly noted. At present, it is impossible to state whether they may be correctly extrapolated to convergence.

Cross-plotting the data from Fig. 6 to a current efficiency-versus-pressure plot, at a series of constant current densities (Fig. 4), produced a set of straight lines on the semi-logarithmic scale, again apparently converging.

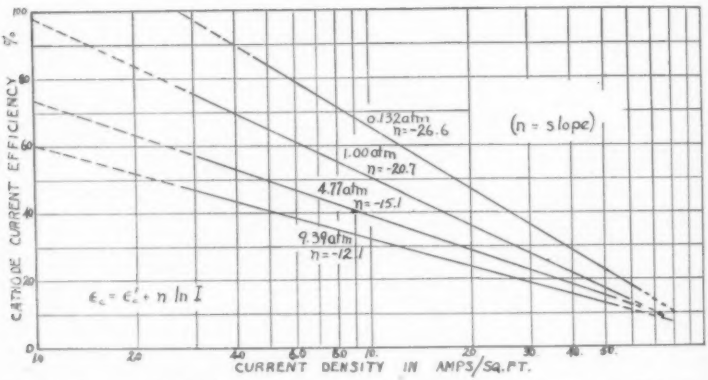

FIG. 6. Corrected plot showing the effect of pressure upon the current efficiency vs. current density relation.

From these two plots, the following general mathematical correlations may be drawn:

$$\epsilon_c = \epsilon_c'' + n \ln I \qquad \text{(from Fig. 6)} \qquad (1)$$

$$\epsilon_c = \epsilon_c'' + m \ln p \qquad \text{(from Fig. 7)} \qquad (2)$$

where:

ϵ_c = current efficiency
ϵ_c' = intercept at unity c.d.
ϵ_c'' = intercept at unity pressure
n = slope of isobar
m = slope of constant c.d. lines

If ϵ_c°, the current efficiency at unity current density and unity pressure, is used, these two may be combined:

$$\epsilon_c = \epsilon_c^\circ + n \ln I + m \ln p \qquad (3)$$

It will be noted that "n" is a function of p, and "m" is a function of I. Accordingly, a plot of slope n versus p and a plot of slope m versus I have

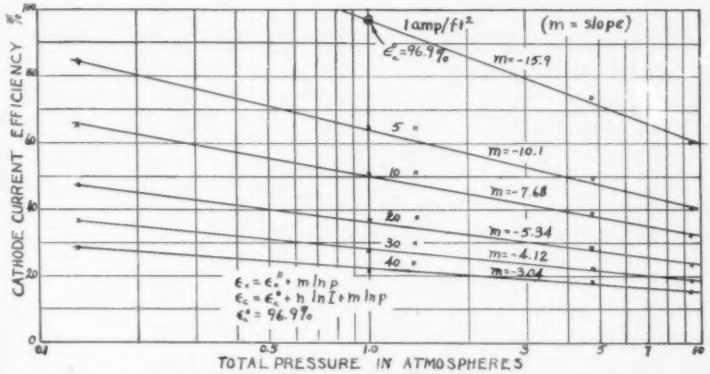

FIG. 7. Current efficiency vs. total pressure at constant current density for a copper cyanide plating bath.

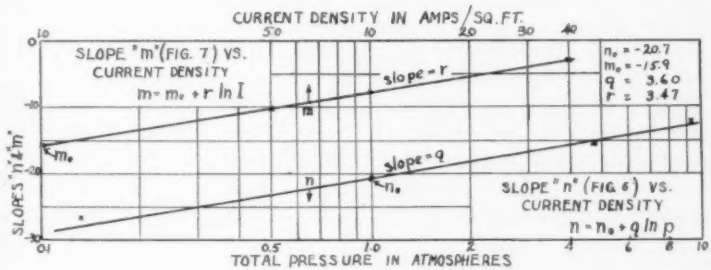
CURRENT DENSITY IN AMPS/SQ.FT.
SLOPE "m" (FIG. 7) VS. CURRENT DENSITY
m = m₀ + r ln I
slope = r
m₀
n₀
slope = q
SLOPE "n" (FIG. 6) VS. CURRENT DENSITY
n = n₀ + q ln p
n₀ = -20.7
m₀ = -15.9
q = 3.60
r = 3.47
SLOPES "n" & "m"
TOTAL PRESSURE IN ATMOSPHERES

FIG. 8

been made in Fig. 8. Both plots are seen to be straight lines on the semi-log scale. The general expressions for these lines are:

$$n = n_0 + q \ln p \tag{4}$$

$$m = m_0 + r \ln I \tag{5}$$

where:

n_0 = intercept of n at unity pressure
m_0 = intercept of m at unity I
q = slope on "n" line
r = slope of "m" line

These constants are evaluated for this system at 50°C. as follows:

$$n_0 = -20.7$$
$$m_0 = -15.9$$

$$q = 3.60$$
$$r = 3.47$$
$$\epsilon_c^0 = 96.9\%$$

Equation (3) may be written in exponential form:

$$e^{\epsilon_c - \epsilon^0} = I^n p^n \tag{6}$$

It should be noted that the extrapolation to unity current density is merely a mathematical convenience and does not represent an extension of the application of this data beyond the limits of the experiment. More than likely, the lines cease to be straight at the lower current densities. There is evidence in the case of the 0.132-atm. line that this does occur. This departure from the linear relationship is similar to that observed in overvoltage curves at low current density.

Four mechanisms suggest themselves in explanation of the effect of pressure upon current efficiency:

(1) Variation of the hydrogen overvoltage with pressure.

(2) Variation of the copper deposition potential with pressure.

(3) Changes in the solution composition, due to displacement of cyanide from solution.

(4) Oxygen depolarization of the hydrogen at the cathode, due to increased oxygen solubility at high pressure.

While it is possible for pressure to have a slight effect on the deposition potential of copper, it is not likely that the change would be of the order of magnitude observed, considering the moderate range of pressures studied.

If any change in the total cyanide content of the solution occurred, there was a loss of cyanide, certainly not a gain. But, after reducing the copper content of the solution to its original value by regeneration, the current efficiencies of the resultant solutions were successively lower. In Fig. 4 and 5, line "b" is the curve of the original solution, and lines "a" and "c" are the curves after the first and second regenerations respectively. Therefore, we conclude that the improvement in efficiency at reduced pressure could not be due to the removal of cyanide from the solution.

To determine whether oxygen elimination had increased the efficiency, a series of runs was made in which oxygen-free nitrogen was bubbled through the solution during electrolysis. The results of these tests are tabulated in Table I. A distinct improvement in efficiency was noted, which might be attributed to:

a. elimination of oxygen

b. increased agitation

c. the thicker plate due to longer time of plating.

Since oxygen elimination was the focus of attention in this test, another run was performed under the same conditions as the last nitrogen runs

except that carbon dioxide-free air was bubbled through. The efficiency was almost identical with the previous nitrogen runs. We may, therefore, eliminate oxygen concentration as the significant mechanism.

We are, moreover, free to draw the conclusion that the hydrogen overvoltage has varied with the total pressure. This suggestion is not new, but the present state of the literature and the generally accepted theories seem to deny it. Hydrogen overvoltage would have to change in such a manner that the total hydrogen potential would become more negative with decreasing pressure at any given current density, thus allowing a greater proportion of the current to be employed in copper deposition.

If this effect exists, it must be great enough to overcome the opposing change in the reversible potential of hydrogen. This potential has been found to follow the Nernst equation very closely (4) (5):

$$E_R = -\frac{RT}{2F} \ln P_{H_2}$$

The similarity in form of this equation to that calculated in this paper for the effect of pressure upon current efficiency is of interest.

By plotting the current in amperes per square foot for the copper deposition and that used for hydrogen deposition against total current density, a form of the current density versus potential curve has been approximated to an arbitrary scale. This has not been included here because, lacking actual potential values, it is of little real value. Work is being performed to supply the potential data, on the basis of which the relative copper and hydrogen curves may be drawn directly. The displacement of the hydrogen curve due to pressure may be readily observed.

It is recommended that further study of the effect of pressure upon hydrogen overvoltage should be performed to determine accurately the magnitude of the effect.

It is unlikely that this improvement in efficiency is sufficient to warrant the use of reduced pressure technique in general copper alkaline-cyanide plating, but in "borderline" baths, where hydrogen evolution prevents plating beyond a thin film, this method may allow further plating. Work of this nature is projected by the Columbia University electrochemical laboratories.

Any discussion of this paper will appear in the discussion section of Volume 94 of the Transactions of the Society.

TABLE OF NOMENCLATURE

e the base of natural logarithms
ϵ the cathode current efficiency of copper deposition
ϵ' the cathode current efficiency (copper) at unity current density for any given pressure.
ϵ'' the cathode current efficiency (copper) at unity pressure for any given current density.

ϵ_c^0 the current efficiency (copper) at unity current density and unity pressure.
I the current density, amperes per square foot.
p the total pressure, atmospheres.
n a constant dependent upon pressure.
n_0 the value on n at unity pressure.
m a constant dependent upon current density.
m_0 the value of m at unity current density.
q, r constants
E_R the reversible potential of hydrogen on the hydrogen scale.
R the gas constant
T the absolute temperature
F the Faraday

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